Dichroism effects in the absorption spectra of Jahn-Teller centers

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A matrix formulation of the moment technique for optical transitions from an orbitally nondegenerate state to a set of close multiplets is developed. Relations are derived for the variation induced by external and internal fields in the spectral moments. These relations are valid for any point group at an arbitrary electron-vibrational coupling and at an arbitrary vibration dispersion law. The Jahn-Teller interaction constants can be determined and the dichroism dispersion curve plotted on the basis of these relations. The theory is used to analyze piezodichroism and electroabsorption of color centers.

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1. INTRODUCTION

If the electrons of an impurity center interact strongly with the Jahn-Teller vibrational modes it is impossible to calculate analytically the shapes of the optical bands, but analytic expressions can be obtained for the moments of the spectrum. When the phonon width of the band masks the splitting of the electron spectrum, these expressions make it possible, by using the observable changes of the moments in dichroism effects, to obtain information on the structure of the energy spectrum, on the symmetry of the electronic states, and on the constants of the interaction with the lattice. This aspect of the method of moments was pointed out first in[1] as applied to the particular case of an F center in an alkali-halide crystal (AHC). However, the formulas given in[1] for the change in the moments under the influence of the perturbing field are not compact and call for a complete analysis of the matrix elements in each particular case.

In this paper we develop a matrix formalism that leads to very general relations for the moments and their variations in an external field; these formulas are valid for any point group of the center, for any symmetry of the perturbation, and for any arbitrary oscillation dispersion law. Besides the general problems of the theory, we consider the application of the theory to piezodichroism, magnetic circular dichroism (MCD), and electroabsorption of color centers.

2. MATRIX FORMULATION OF THE METHOD OF MOMENTS

We consider an impurity center having an orbitally nondegenerate electronic ground state. It is assumed that this state satisfies the adiabatic-approximation criteria. The symmetry group G of the corresponding equilibrium configuration of the crystal environment will be called the symmetry group of the center. Neglecting effects due to population of the excited electronic states and their mixing with the ground state by the electron-vibrational interaction, the following expression was obtained in[2] for the form function of the light absorption band:

$$F_\eta(\Omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(-i\Omega t)\,\mathbf{d}_\eta^+\exp\left(\frac{i\mathbf{H}_e t}{\hbar}\right)\langle\mathbf{U}(t)\rangle_L\mathbf{d}_\eta\,dt, \tag{1}$$

where Ω is the frequency of the light, η is the polarization index, $\mathbf{H}_e$ is the Hamiltonian of the electrons of the local center in the quenched equilibrium ground state configuration, $\mathbf{H}_e$ and $\mathbf{U}$ are the matrices of the electronic Hamiltonian and of the evolution operator in the basis of all the excited states $|\Gamma\gamma\rangle$ of the Hamiltonian H_e (Γ is an irreducible representation of the group G and γ is the index of its row), and $\mathbf{d}_\eta$ is a single-column transition dipole-moment matrix made up of the elements $\langle\Gamma\gamma|\mathbf{d}_\eta|A\rangle$ (A is the ground state). Formula (1) is "exact," since it takes into account all the excited states; actually the basis is limited only to those excited states which make a real contribution to the observed band. The evolution operator is represented in the usual manner:

$$\mathbf{U}(t)=T\exp\left[\frac{i}{\hbar}\int_0^t\mathbf{H}_{eL}(-\tau)\,d\tau\right], \tag{2}$$
$$\mathbf{H}_{eL}(\tau)=\exp(i\mathbf{H}_0\tau/\hbar)\mathbf{H}_{eL}\exp(-i\mathbf{H}_0\tau/\hbar),$$

where $H_0=H_e+H_L$ is the zero-order Hamiltonian with separable variables, for which (see[2]) the adiabatic wave functions of the electronic ground state are exact eigenfunctions; H_L is the free-photon Hamiltonian, and finally $\mathbf{H}_{eL}$ is the Hamiltonian of the electron-phonon interaction in the linear approximation

$$\mathbf{H}_{eL}=\sum_\varkappa\mathbf{v}_\varkappa q_\varkappa, \tag{3}$$

in which the normal coordinates $q_\varkappa$ of the crystal oscillations are reckoned from the equilibrium configuration of the initial state, and $\langle\ldots\rangle_L$ denotes statistical averaging over the vibrational states:

$$\langle B\rangle_L=Z_L^{-1}\,\mathrm{Sp}\,[\exp(-H_L/kT)B],\quad Z_L=\mathrm{Sp}\exp(-H_L/kT). \tag{4}$$

We separate from H_e the unit part, representing $\mathbf{H}_e$ in the form

$$\mathbf{H}_e=\hbar(\Omega_0\mathbf{1}+\mathbf{W}),\quad \mathrm{Sp}\,\mathbf{W}=0, \tag{5}$$

where $\hbar\Omega_0$ is the center of gravity of the considered group of levels, while $\mathbf{W}$ includes both the initial splitting and the splitting due to the external perturbing field.

To calculate the moments we assume the following normalization to unity area (zeroth moment) of the distribution (1)

$$\int_{-\infty}^{\infty} F_\eta(\Omega)\,d\Omega=\mathbf{d}_\eta^+\mathbf{d}_\eta=1. \tag{6}$$

For the first moment (center of gravity) of the band we obtain

$$\bar\Omega_\eta=\int_{-\infty}^{\infty} F_\eta(\Omega)\,\Omega\,d\Omega=\Omega_0+\Delta\bar\Omega_\eta,\quad \Delta\bar\Omega_\eta=\mathbf{d}_\eta^+\mathbf{W}\mathbf{d}_\eta. \tag{7}$$

Defining the n-th centered moment by the relation

$$\langle\Omega^n\rangle_\eta=\int_{-\infty}^{\infty} (\Omega-\bar\Omega_\eta)^n F_\eta(\Omega)\,d\Omega \tag{8}$$

and substituting $F_\eta(\Omega)$ from (1), we obtain after some transformations

$$\langle\Omega^n\rangle_\eta=\sum_{k=0}^{n}\binom{n}{k}\ \mathbf{d}_\eta^+(\mathbf{W}-\Delta\Omega_\eta 1)^{n-k}\boldsymbol{\sigma}_k\mathbf{d}_\eta, \tag{9}$$

where $\binom{n}{k}$ are the binomial coefficients. The quantities

$$\boldsymbol{\sigma}_k=\left\langle\frac{d^k}{d(it)^k}\mathbf{U}(t)\Big|_{t=0}\right\rangle_L \tag{10}$$

will be called the matrices of the elementary moments. We note that $\sigma_0=1$ and $\sigma_1=0$.

The moments of the band (9) have the structure of quantum-mechanical mean values in which the single-column matrices $\mathbf{d}_\eta$ serve as "state vectors." Further simplification is obtained with the aid of the formalism of irreducible tensor operators.[3,4] To this end we break up the electron operators $\mathbf{v}_\varkappa$ into parts corresponding to the irreducible vibrational representations $\bar\Gamma$ of the group G[5]:

$$\mathbf{v}_\varkappa=\sum_{\bar\Gamma\bar\gamma}\left(\frac{\hbar}{M\omega_\varkappa}\right)^{1/2} a_\varkappa(\bar\Gamma\bar\gamma)\,\mathbf{V}_{\bar\Gamma\bar\gamma}, \tag{11}$$

where M is the normalization mass of the crystal, $\mathbf{V}_{\bar\Gamma\bar\gamma}$ are irreducible tensor operators on the group G, and $a_\varkappa(\bar\Gamma\bar\gamma)$ are the coefficients of the expansion of the symmetrized displacements of the atoms of the defect region of the crystal in terms of the normal vibrations, and satisfy the orthogonality condition

$$\int do_\varkappa a_\varkappa(\bar\Gamma\bar\gamma)\,a_\varkappa(\bar\Gamma'\bar\gamma')=b_\varkappa(\bar\Gamma)\,\delta_{\bar\Gamma\bar\Gamma'}\delta_{\bar\gamma\bar\gamma'}, \tag{12}$$

where the integral is taken over the directions of the phonon wave vectors.

Leaving out the details of the transformations, we present an expression for σ_k at $k=2$ and 3 ($\beta_\varkappa=\hbar\omega_\varkappa/kT$):

$$\boldsymbol{\sigma}_2=\frac{1}{2M\hbar}\sum_\varkappa\sum_{\bar\Gamma}\frac{b_\varkappa(\bar\Gamma)}{\omega_\varkappa}\operatorname{cth}\frac{\beta_\varkappa}{2}\sum_{\bar\gamma}\mathbf{V}_{\bar\Gamma\bar\gamma}^+\mathbf{V}_{\bar\Gamma\bar\gamma}\equiv\sum_{\bar\Gamma}\boldsymbol{\sigma}_2(\bar\Gamma), \tag{13}$$

$$\boldsymbol{\sigma}_3=\boldsymbol{\sigma}_3^{(1)}+\boldsymbol{\sigma}_3^{(2)}, \tag{14}$$

$$\boldsymbol{\sigma}_3^{(1)}=\frac{1}{2M\hbar}\sum_\varkappa\sum_{\bar\Gamma}b_\varkappa(\bar\Gamma)\sum_{\bar\gamma}\mathbf{V}_{\bar\Gamma\bar\gamma}^+\mathbf{V}_{\bar\Gamma\bar\gamma}, \tag{15}$$

$$\boldsymbol{\sigma}_3^{(2)}=\frac{1}{2M\hbar}\sum\sum_{\bar\Gamma}\frac{b_\varkappa(\bar\Gamma)}{\omega_\varkappa}\operatorname{cth}\frac{\beta_\varkappa}{2}\sum_{\bar\gamma}\mathbf{V}_{\bar\Gamma\bar\gamma}^+[\mathbf{W},\mathbf{V}_{\bar\Gamma\bar\gamma}]. \tag{16}$$

Inasmuch as the chosen basis includes the exact eigenfunctions and eigenvalues of the operator W, the transition to the limited basis is not connected with smallness of the perturbation[1)] of W. However, on going to a limited basis we neglect the matrix elements of the electron-phonon interaction between the states of the chosen basis and the remaining (not accounted for) states. Physically, the criterion of this approximation is the absence of any noticeable overlap between the considered band and the remaining absorption bands of the crystal. We emphasize that if the band has a structure due to the splitting in the electronic spectrum, then formula (9) pertains to the entire band and cannot be used for its individual structure elements.

3. CHANGE OF MOMENTS IN EXTERNAL FIELD

We consider first an actual particular case in which, at a chosen polarization $\eta=\pi$ of the light, a transition to a single level $\Gamma=\Pi$ is allowed. Since the matrix W is diagonal in the chosen basis, the state vector $\mathbf{d}_\pi$ with the single nonzero component is an eigenvector of W and belongs according to (6) and (7) to the eigenvalue $\Delta\bar\Omega_\pi$. It is easily seen that in this case the only nonzero term in the binomial sum (9) is the one with $k=n$, and we obtain

$$\langle\Omega^n\rangle_\pi=\mathbf{d}_\pi^+\boldsymbol{\sigma}_n\mathbf{d}_\pi. \tag{17}$$

Thus, the moments of the band are obtained by simple averaging of the corresponding matrices (10). Putting $\mathbf{W}=\mathbf{W}_0+\mathbf{W}_e$, where $\mathbf{W}_0$ is responsible for the "intrinsic" splitting of the center levels and W_e is the interaction with the external field, we introduce the point symmetry group G_0 of the Hamiltonian $\mathbf{W}_0$. The group G is obviously a subgroup of the complete group G_0. We shall henceforth neglect the matrix elements of the external-perturbation operator between the states of the chosen basis and the unaccounted-for states in comparison with the corresponding energy gaps, and in this sense we regard the perturbation as small. The wave functions that diagonalize $\mathbf{W}_e$ are then linear combinations of the eigenfunctions of the operator $\mathbf{W}_0$, and by virtue of the unitary invariance of formulas (9) and (17) we can use wave functions that transform in accordance with the irreducible representations of the group G_0 as the basis. We note, however, that for the electron-phonon interaction the transition from G_0 to G does not reduce, generally speaking, to a formal reduction of the tensor operators $\mathbf{V}_{\bar\Gamma\bar\gamma}$(2), since there exist physical mechanisms that make the parameters of the phonon spectrum and of the electron-phonon interaction dependent on the external field. These effects, as usual, are assumed to be small and are disregarded in this paper. As a result, the dependence of the moments of the spectrum on the perturbations is restricted to terms that contain W explicitly. In particular, σ_2 and $\sigma_3^{(1)}$ do not depend on the external field. In the basis G_0, naturally, the perturbation $\mathbf{W}_e$ is not diagonal and can be expanded in irreducible tensor operators of the group G_0.

We confine ourselves below to the case when a single tensor operator $W(\Lambda\lambda)$ differs from zero, and represent its matrix, with the aid of the Wigner-Eckart theorem, in the form[3]

$$\langle\Gamma\gamma|W_e(\Lambda\lambda)|\Gamma'\gamma'\rangle=\langle\Gamma\|W_e(\Lambda)\|\Gamma'\rangle\begin{pmatrix}\Gamma\Gamma'\Lambda\\ \gamma\gamma'\lambda\end{pmatrix}, \tag{18}$$

where $\langle\|\cdots\|\rangle$ is the reduced matrix and

$$\begin{pmatrix}\Gamma_1 & \Gamma_2 & \Gamma_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{pmatrix}$$

is the 3Γ-symbol of the point group. In the derivation of the subsequent formulas for the moments we use the known relations for the 3Γ symbols of point groups.[3]

For the change of the first moment of the band under the influence of the external field we obtain from (7)

$$\Delta\bar{\Omega}_\pi=\langle\Pi\|W_e(\Lambda)\|\Pi\rangle\begin{pmatrix}\Pi\Pi\Lambda\\ \pi\pi\lambda\end{pmatrix}. \tag{19}$$

For the second moment of the band, which does not depend in this case on the external field, we get

$$\langle\Omega^2\rangle_\pi=\sum_{\bar{\Gamma}}\sigma_2(\bar{\Gamma}), \tag{20}$$

$$\sigma_2(\bar{\Gamma})=\frac{1}{2M\hbar[\Pi]}\sum_{\varkappa}\frac{b_\varkappa(\bar{\Gamma})}{\omega_\varkappa}\operatorname{cth}\frac{\beta_\varkappa}{2}\mathbf{V}_{\bar{\Gamma}}^{+}\mathbf{I}\mathbf{V}_{\bar{\Gamma}}, \tag{21}$$

where $\mathbf{V}_{\bar{\Gamma}}$ is a matrix made up of the reduced matrix elements $\langle\pi\|V_{\bar{\Gamma}}\|\Gamma\rangle$, $[\Pi]$ is the dimensionality of the representation of Π, $\mathbf{I}$ is a diagonal matrix of the form $\langle\Gamma|I|\Gamma'\rangle=(-1)^{j(\Gamma)}\delta_{\Gamma\Gamma'}$, and $j(\Gamma)$ is the quasi-moment of the representation Γ.[3]

It follows from (21) that a contribution to the second moment is made not only by the vibrational representations contained in the expansion of the symmetrized square $[\Pi^2]$, but also by those vibrations that mix the final electronic state Π with other excited states. The perturbation-independent matrix $\sigma_3^{(1)}$ (15) has a structure that is perfectly similar to (20). For the change of the third moment under the influence of the external field we obtain

$$\Delta\langle\Omega^3\rangle_\pi=\frac{(-1)^{j(\Lambda)}}{2M\hbar}\begin{pmatrix}\Pi\Pi\Lambda\\ \pi\pi\lambda\end{pmatrix}\sum_{\varkappa,\bar{\Gamma}}\frac{b_\varkappa(\bar{\Gamma})}{\omega_\varkappa}\mathbf{V}_{\bar{\Gamma}}^{+}\mathbf{I}\overline{\mathbf{W}}_e\mathbf{I}\mathbf{V}_{\bar{\Gamma}}-\Delta\bar{\Omega}_\pi\sum_{\bar{\Gamma}}\sigma_2(\bar{\Gamma}),$$
$$\langle\Gamma|\overline{W}_e|\Gamma'\rangle=\langle\Gamma\|W_e(\Lambda)\|\Gamma\rangle\begin{Bmatrix}\Lambda\Pi\Pi\\ \bar{\Gamma}\Gamma'\Gamma\end{Bmatrix}, \tag{22}$$

$\begin{Bmatrix}\cdots\\ \cdots\end{Bmatrix}$ is the 6Γ-symbol of the point group.

In the case of a transition from an isolated degenerate level, formula (22) takes the simpler form

$$\Delta\langle\Omega^3\rangle_\pi=\Delta\bar{\Omega}_\pi\sum_{\bar{\Gamma}}a_{\bar{\Gamma}}\sigma_2(\bar{\Gamma}),$$
$$a_{\bar{\Gamma}}=[\Pi](-1)^{j(\bar{\Gamma})+j(\Lambda)}\begin{Bmatrix}\Pi\Pi\Lambda\\ \Pi\Pi\bar{\Gamma}\end{Bmatrix}-1. \tag{23}$$

Thus, the change of the third moment turns out to be proportional to the change of the first, the proportionality coefficient being a linear combination of the components $\sigma_2(\bar{\Gamma})$ of the second moment. The connection between the coefficients $a_{\bar{\Gamma}}$ and the 6Γ symbols, which is established by relation (23), makes it possible to find these coefficients from tables[3] for a center of any symmetry and any external field. The quantity $\Delta\langle\Omega^3\rangle/\Delta\bar{\Omega}$ can be calculated directly from the experimental data on the spectra of absorption in an external field. By choosing external fields of different physical nature and symmetry, it is possible to obtain with the aid of (23) a system of equations for the unknown components $\sigma_2(\bar{\Gamma})$ of the second moment. The number of unknowns is equal to the number of Jahn-Teller vibrational representations $\bar{\Gamma}\in[\Pi^2]$, $\Pi\times\Gamma$. On the other hand, the number of equations is determined in accordance with (19) by the number of representations $\Lambda\in\Pi\times\Pi$, $\Pi\times\Gamma$, so that it is in any case not less than the number of the unknowns. It is easy to show that the joint action of several perturbations of different symmetry does not lead to new linearly-independent equations.

The linear connection between the changes of the third and first moments takes place not only for the transition to an isolated multiplet, but also in some more general cases, by virtue of the special selection rules. We illustrate this with an F center as an example (transition $A_{1g}\to T_{1u}$ in the group $G_0=O_h$), including in the basis of the matrix representation, besides the final excited state T_{1u}, also the closely-lying excited level A_{1g}.[3)] In this case $\bar{\Gamma}=A_{1g}$, E_g, T_{2g}, T_{1u}; the first three are contained in $[T_{1u}^2]$, and the last one mixes T_{1u} and A_{1g}. It is seen directly from (16) that the fully-symmetrical modes A_{1g} make no contribution to the change of the third moment. To determine the contribution of the Jahn-Teller modes E_g and T_{2g} and of the odd "pseudo-Jahn-Teller" modes T_{1u} we obtain three equations by using as the perturbation tetragonal and trigonal uniaxial compression ($\Lambda=E_g$ and $\Lambda=T_{2g}$, respectively) as well as the magnetic field ($\Lambda=T_{1g}$). With the aid of (22) and the tables of the 6Γ symbols[3] we obtain directly

$$\Delta\langle\Omega^3\rangle_{tetr}=-\Delta\bar{\Omega}_{tetr}[{}^3/{}_2\sigma_2(T_2)+\sigma_2(T_{1u})], \tag{24}$$

$$\Delta\langle\Omega^3\rangle_{trig}=-\Delta\bar{\Omega}_{trig}[{}^1/{}_2\sigma_2(T_2)+{}^3/{}_2\sigma_2(E)+\sigma_2(T_{1u})], \tag{25}$$

$$\Delta\langle\Omega^3\rangle_{\mathrm{MCD}}=-\Delta\bar{\Omega}_{\mathrm{MCD}}[{}^3/{}_2\sigma_2(T_2)+{}^3/{}_2\sigma(E)+\sigma_2(T_{1u})]. \tag{26}$$

Expressions (24) and (25) are valid for each of the two polarizations of light, perpendicular or parallel to the deformation axis; accordingly, (26) is valid for each of the two circular polarizations in a plane perpendicular to the magnetic field. After obtaining $\sigma_2(\bar{\Gamma})$ ($\bar{\Gamma}=E_g$, T_{2g}, T_{1u}) from (24)–(26), we can determine $\sigma_2(E)$ by merely using the additivity relation (13) for the components of the second moment.

The relations between the changes of the third and first moments, without allowance for the contribution of the A_{1g} level and accordingly the T_{1u} vibrations, were first obtained in[1] and were subsequently used many times to analyze experimental data on piezodichroism[8,9] and MCD[10,11] of F centers. The question of the role of the T_{1u} vibrations is of exceptional interest. In all the cited papers, the contribution of these vibrations was completely disregarded, yet it was proposed by Ham[12] that the contribution of the T_{1u} vibrations is dominant. Unfortunately, the papers on the MCD of F centers in alkali-halide crystals contain no analysis of the change of the third moment, so that the values

TABLE I.

$\overline{\Gamma}$	A_1	E	T_2	T_2*
$\sigma_2(\overline{\Gamma})/\langle\Omega^2\rangle$	0.025	0.159	0.36	0.456

*The last column pertains to the pseudo-Jahn-Teller part of $_2(T)_2$.

$\sigma_2(T_2)$ and $\sigma_2(E)$, obtained in[8] from piezodichroism, require additional verification.[4)] A detailed analysis of MCD was carried out in[14] for an F center in CaO; the piezodichroism of the same centers was investigated in[15], but no data are given there on the change of the third moment. From this point of view, another paper[16] is of interest, in which the F center in $SrCl_2$ (group T_d, transition $A_1 \rightarrow T_2$) was investigated by both mentioned methods. A noticeable difference between the Jahn–Teller part of the second moment (~100%) obtained from piezodichroism and the value obtained from MCD (~80%) was observed (but not discussed). This contradiction is eliminated with the aid of formulas (24)–(26) by taking into account the mixing contribution of the T_2 vibrations. The relative contribution of vibrations of different symmetry to the second moment of the F band in the $SrCl_2$ crystal is listed in the table. From the data in Table I it is seen that the "mixing" T_2 vibration and the Jahn–Teller T_2 and E vibrations make approximately equal contributions to the half-width of the F band.

Thus, on the one hand, the pseudo-Jahn–Teller vibrations must be taken into account, in the analysis of the shape of the F band and its variations in dichroism effects, and on the other hand, one cannot neglect the contribution of the Jahn–Teller vibrations in the analysis of effects considered in[12].

4. ELECTROABSORPTION OF *F* CENTERS

The choice of the external perturbation, in which a transition to only one of a group of excited levels is allowed for each polarization, excludes, as can be seen directly from (17), the possibility of determining the energy gaps in the electronic spectrum from the observed changes of the moments. To solve this problem it is necessary to choose a perturbation that mixes the electronic states of the group G_0. In particular, to determine the energy of the even excited states of any F centers it is necessary to use the electroabsorption method.[17–21] We include in the basis of the matrix representation, besides the $2p$-like (T_{1u}) state, also the $2s$-like (A_{1g}) state responsible for the quadratic Stark effect at $\mathbf{d}_\tau \parallel \mathbf{E}$, and the $3d$-like states (E_g and T_{2g} levels of cubic field) which lead to the Stark effect at $\mathbf{d}_\tau \perp \mathbf{E}$ (Fig. 1). Since the transition in the group C_{4v} ($W_e \neq 0$) is allowed for each polarization into two excited levels, the conditions for the applicability of (17) are not satisfied, and the moments of the band should be calculated from the general formula (9). Returning to the G_0 basis, we obtain for the first moment in accordance with formula (7)

$$\bar{\Omega}_\pi = \Omega_0 + \varepsilon(T_{1u}), \tag{27}$$

where $\varepsilon(\Pi)$ is the level energy reckoned from the center of gravity of the above-mentioned group of excited levels.

For the change produced in the higher-order moments by the electric field we obtain

$$\Delta\langle\Omega^2\rangle_\pi = \mathbf{W}_e^{+}\mathbf{I}_\pi\mathbf{W}_e, \tag{28}$$

$$\Delta\langle\Omega^3\rangle_\pi = \mathbf{W}_e^{+}\mathbf{W}_{0\pi}\mathbf{W}_e - \mathbf{W}_e^{+}\mathbf{I}_\pi\mathbf{W}_e\varepsilon(T_{1u}), \tag{29}$$

$$\langle\Gamma|I_\pi|\Gamma'\rangle = \delta_{\Gamma\Gamma'}(-1)^{j(\Gamma)}\sum_\gamma\begin{pmatrix}\Gamma\Pi\Lambda\\ \gamma\pi\lambda\end{pmatrix}^2, \tag{30}$$

$$\langle\Gamma|W_{0\pi}|\Gamma'\rangle = \Delta(\Gamma)\langle\Gamma|I_\pi|\Gamma'\rangle, \quad \Delta(\Gamma) = \varepsilon(\Gamma) - \varepsilon(T_{1u}). \tag{31}$$

It follows from these relations that the first moment of the electroabsorption band does not depend on the external-field intensity, and the changes of the higher-order moments depend on this field quadrically. It is important that the changes of the second and third moments do not depend on the electron-phonon interaction.

The ranks of the matrices in (28)–(31) are determined only by the number of the levels taken into account, regardless of their degeneracy multiplicity. In our case ($\Gamma = T_{1u}$, A_{1g}, E_g, T_{2g}) these matrices take the form

$$\mathbf{W}_{0\parallel} = \frac{1}{3}\begin{vmatrix}0 & 0 & 0 & 0\\ 0 & \Delta_1 & 0 & 0\\ 0 & 0 & \Delta_2 & 0\\ 0 & 0 & 0 & 0\end{vmatrix}, \quad \mathbf{W}_e = \begin{vmatrix}0\\ \zeta_1\\ \zeta_2\\ \zeta_3\end{vmatrix}, \quad \zeta_i = \langle T'_{1u}\|W_e\|\Gamma_i\rangle,$$

$$\mathbf{W}_{0\perp} = \frac{1}{6}\begin{vmatrix}0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & \Delta_3\end{vmatrix}, \quad \mathbf{I}_\parallel = \frac{1}{3}\begin{vmatrix}0 & 0 & 0 & 0\\ 0 & 1 & 0 & 0\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0\end{vmatrix}, \quad \mathbf{I}_\perp = \frac{1}{6}\begin{vmatrix}-1 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\end{vmatrix}. \tag{32}$$

Substitution in (28) and (29) yields

$$\Delta\langle\Omega^2\rangle_\parallel = {}^1/_3(\zeta_1^2 + \zeta_2^2), \quad \Delta\langle\Omega^2\rangle_\perp = {}^1/_6\zeta_3^2, \tag{33}$$

$$\Delta\langle\Omega^3\rangle_\parallel = {}^1/_3(\Delta_1\zeta_1^2 + \Delta_2\zeta_2^2), \quad \Delta\langle\Omega^3)_\perp = {}^1/_6\Delta_3\zeta_3^2. \tag{34}$$

It follows from these equations that by confining ourselves to the even level A_{1g} closest to T_{1u} we can estimate the corresponding energy gap from the relation

$$\Delta_1 = \Delta\langle\Omega^3\rangle_\parallel/\Delta\langle\Omega^2\rangle_\parallel. \tag{35}$$

Unfortunately, the change of the third moment was not determined in the cited experimental papers. In addition, when account was taken of the $3d$ level responsible for the absorption, the system (33) and (34) at $\mathbf{d}_\tau \perp \mathbf{E}$ contains more parameters than equations. We therefore used the method of reconstructing the spectrum from the moments.[22,23] Since the F band in alkali-halide crystals is close to Gaussian, we describe it by the known Edgeworth formula (see e.g., [2]) confining ourselves in the expansion of $F(\Omega)$ in Chebyshev-Hermite

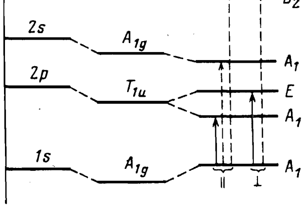

FIG. 1. Level scheme of F center in electric field. The dashed lines designate transitions that are allowed in the presence of an electric field. The symbols ⊥ and ∥ correspond to light polarized perpendicular and parallel to the electric field.

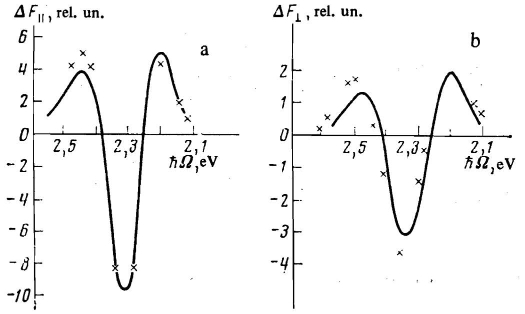

FIG. 2. Electroabsorption of *F* center: a—light polarization parallel to the electric field, b—light polarization perpendicular to electric field. Solid—theory, points—experiment.

polynomials to terms up to third order inclusive. We then obtain for the electroabsorption

$$\Delta F(\Omega)=\frac{\partial F(\Omega)}{\partial\langle\Omega^2\rangle}\bigg|_{E=0}\Delta\langle\Omega^2\rangle+\frac{\partial F(\Omega)}{\partial\langle\Omega^3\rangle}\bigg|_{E=0}\Delta\langle\Omega^3\rangle. \tag{36}$$

The best agreement between the theoretical curve (36) and the experimental data on the dispersion of the electroabsorption, in the case of parallel[19] and perpendicular[21] polarization (Fig. 2), is reached at the following values of the parameters: $\Delta_1=0.036$ eV, $\Delta_2=0.11$ eV, $\Delta_3=0.13$ eV, and $(\zeta_2/\zeta_1)^2=0.27$. The discrepancy between theory and experiment in the short-wave region is due to the influence of the unaccounted-for *K* absorption band.

Substituting the numerical values of Δ_i and ζ_2/ζ_1 in (33), we can estimate the matrix elements $\langle T_{1u}|z|\Gamma_i\rangle = z_i$ from the measured values of the second moment. The experimental values of $\Delta\langle\Omega^2\rangle_\perp$ are given in[19,21] and those of $\Delta\langle\Omega^2\rangle_\parallel$ in[20]. Using these data, as well as the Lorentz formula for the effective field, we obtain for the *F* center of KCl

$$z_1\approx 1.0 \text{ at. un.} \quad z_2\approx 0.5 \text{ at. un.} \quad z_3\approx 0.65 \text{ at. un.}$$

These results differ from those obtained earlier.[19,20,24] The causes of the difference are the following. No account was taken in[24] of the contribution of the forbidden $1s\to 2s$ transition to the electroabsorption. This is permissible if Δ_1 greatly exceeds the width of the *F* band, which apparently is not the case. In[19,20] the theoretical curve was approximated by a superposition of Gaussians in accordance with the number of accounted-for at ($\mathbf{E}\neq 0$) allowed transitions. This approach, however, is wrong even in the zero approximation, since it leads, in contrast to the exact results of the theory (28), to a dependence of the change of the second moment on the electron-phonon interaction (see formula (11) of[19]).

In[25,26] are given the results of an experimental investigation of the electroabsorption in the *M* band of alkali-halide crystals; this absorption is connected with the transition ${}^1A_{1g}\to{}^1B_{1u}$ in the F_2 center (point group D_{2h}). The electroabsorption is due to the excited ${}^1A'_{1g}$ level and is apparently the only method of its detection. This problem is solved in[26] by the method of[24], i.e., under the assumption that the transitions ${}^1A_{1g}\to{}^1A'_{1g}$ and ${}^1A_{1g}\to{}^1B_{1u}$ correspond to isolated bands. The question of the position of the ${}^1A'_{1g}$ level can, however, not be regarded as completely solved; it is desirable to compare the data on the electroabsorption in the *M* band with an alternate variant of the theory (in the case of close levels). It is easy to show that relation (35) (where $\Delta=\varepsilon(A'_{1g})-\varepsilon(B_{1u})$ and $\mathbf{E}\parallel C_2$) takes place also for the F_2 center, so that to analyze the spectrum it is necessary to determine the changes of the second and third moments. No such data have been published as yet.

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[1] The particular case of weak perturbations was considered by Honma.[6]

[2] We retain the symbols Γ and $\overline{\Gamma}$ for the irreducible representations (electronic and vibrational, respectively) of the group G_0.

[3] We neglect the spin-orbit interaction, which is small for *F* centers in alkali-halide crystals.[7]

[4] Henry[13] indicates that the data on MCD agree with those on piezodichroism for *F* centers in alkali-halide crystals. If this is true, then the contribution of the T_{1u} vibrations is negligibly small.

1. C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137A, 583 (1965).
2. Yu. E. Perlin and B. S. Tsukerblat, Éffekty élektronno-kolebatel'nogo vzaimodeĭstviya v opticheskikh spektrakh primesnykh paramagnitnykh ionov (Effects of Electron-Vibrational Interaction in Optical Spectra of Impurity Paramagnetic Ions), Kishinev, Shtiintsa, 1974; in: Spektroskopiya kristallov (Spectroscopy of Crystals), Nauka, 1975, p. 61.
3. J. S. Griffith, The Irreducible Tensor Method for Molecular Symmetry Groups, Prentice Hall, 1962.
4. U. Fano and G. Racah, Irreducible Tensorial Sets, A. P., New Jersey, 1959.
5. Yu. E. Perlin, B. S. Tsukerblat, and E. I. Perepelitsa, Zh. Eksp. Teor. Fiz. 62, 2265 (1972) [Sov. Phys. JETP **35**, 1185 (1972)].
6. A. Honma, J. Phys. Soc. Japan **24**, 1082 (1968).
7. P. Y. Smith, Phys. Rev. **137A**, 574 (1965).
8. S. E. Schnatterly, Phys. Rev. **140A**, 1364 (1965).
9. R. E. Hetrick, Phys. Rev. **188**, 1392 (1969).
10. N. V. Karlov, J. Margerie, and Y. Merle d'Aubigné, J. Phys. Radium **24**, 717 (1963).
11. J. Mort, F. Lüty, and F. C. Brown, Phys. Rev. **137A**, 566 (1965).
12. F. S. Ham, Phys. Rev. **138**, 2926 (1973); F. S. Ham and U. Grevsmühl, *ibid.*, 2945.
13. C. H. Henry, Phys. Rev. **140A**, 265 (1965).
14. Y. M. d'Aubigné and A. Roussel, Phys. Rev. **133**, 1421 (1971).
15. J. Duran, Y. Merle d'Aubigné, and R. Romenstain, J. Phys. C **5**, 2225 (1972).
16. M. Billardon, J. Duran, S. Lefraut, and L. Taurel, Phys. Status Solidi **58b**, 673 (1973).
17. G. Chiarotti, N. M. Grassano, and R. Rossei, Phys. Rev. Lett. **17**, 1043 (1966).
18. C. R. Rhyner and J. R. Cameron, Phys. Rev. **169**, 710 (1969).
19. G. Chiarotti, N. M. Grassano, G. Margaritondo, and R. Rossei, Nuovo Cimento **64B**, 159 (1969).
20. M. Bonciani, N. M. Grassano, and R. Rossei, Phys. Rev. **138**, 5855 (1973).
21. M. Bonciani and N. M. Grassano, Phys. Status Solidi **67b**, 371 (1975).
22. Yu. E. Perlin, L. S. Kharchenko, and B. S. Tsukerblat, Fiz.

Tverd. Tela (Leningrad) **11**, 1065 (1965) [Sov. Phys. Solid State **11**, 869 (1965)].

[23] Yu. E. Perlin and L. S. Kharchenko, *ibid.*, 1997 (1969) [1610 (1970)].

[24] Yu. E. Perlin and E. Yu. Perlin, *ibid.*, 3417 [2871].

[25] L. A. De Werd, Phys. Status Solidi **52**, 207 (1972).

[26] V. A. Krylov, V. N. Medvedev, and K. Yu. Fridland, in: Lyuminestsentnye materialy i osobo chistye veshchestva (Luminescent Materials and Highly Purified Substances), No. 11, Stavropol', 1974, p. 101.

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Oscillations of the critical temperature and resistance in lamellar thin-film vanadium-carbon structures

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The superconducting properties of vanadium-carbon sandwiches with vanadium layers $d_{\rm V} = 100$ Å thick and variable thickness carbon liners are studied. The thickness of the carbon liners was varied between 0 and 100 Å. The investigations are performed with samples having one, two, and five vanadium layers. The dependence of the sandwich superconducting temperature T_c on the carbon liner thickness is oscillatory, the oscillations being particularly pronounced for the samples with two layers. The first peak on the $T(d_{\rm C})$ curve ($d_{\rm C}$ is the thickness of the carbon coating) occurs at $d_{\rm C} = 3$ Å for single-layer samples (vanadium film with carbon coating of variable thickness). In two- and five-layer sandwiches the first peak is observed for a carbon layer thickness of 5 Å. A correlation is obtained between the critical temperature and the quantities R_{300}/R_n, ρ_{300}, and ρ_n for multilayer samples.

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We have previously reported[1,2] observation of an oscillatory dependence of the critical temperature of films of a number of superconducting metals on the thickness of a diamond coating. The oscillations took place at very small carbon coatings ($d_{\rm C} < 20$ Å) and for sufficiently thin ($d < 300$ Å) metallic layers. Quite recently, Sixl[3] reported observation of a similar behavior of the critical temperature of thin aluminum films as a function of the thickness of a silicon-oxide coating. Although the aluminum films were obtained by another method and the coating was of a different material, the general laws governing the $T_c(d_{\rm C})$ dependence were the same as in our experiments. We have continued the investigations on vanadium films coated with carbon, and also studied the effect of a thin dielectric layer (C) of variable thickness on the properties of metallic vanadium film in layered sandwich-type systems.

In the method used to produce the samples, the sandwich structure has a number of advantages over a superconductor coated with a dielectric of variable thickness. Thus, in the case of a sandwich the sample can be covered from above a thick protective dielectric film, and this excludes completely the possibility of oxidation of the investigated metallic layer. In addition, in the layered sample the thin dielectric layer borders upon two identical metallic layers, so that the action of the dielectric on the superconductor becomes more effective. All this gives grounds for hoping to obtain, in the case of a sandwich, a more distinct oscillatory dependence of the properties of the metallic layer on the thickness of the dielectric.

PREPARATION OF SAMPLES AND MEASUREMENT PROCEDURE

The sample were prepared in a high-vacuum ion-evaporation installation described by us in[2]. The evaporation was carried out in spectrally pure krypton, the working pressure of which was 5×10^{-6} Torr. The discharge current was 1 mA at 4 kV in a magnetic field 0.7 kOe. During the sputtering time all the parts of the working chamber and the substrate had a temperature close to that of liquid nitrogen.

The film thickness was calculated from the evaporation rate and evaporation time. The evaporation rate of each material was determined with the aid of control samples 1000 Å thick. The thicknesses of these samples were determined by an interference method. The error in the determination of the investigated films did not exceed 5% in the entire range of thicknesses. The film growth rates were 10 Å/min for vanadium and 2 Å/min for carbon films1). The determination of the growth rate was repeated after several evaporation experiments.

The raw materials for the cathode were metallic vanadium and graphite of purity not worse than 99.94%. The investigated samples were rectangular in shape and measured 5×9 mm. The substrates were polished glass plates into which platinum-wire leads were sealed. To exclude edge effects, the edges of the films were trimmed with a diamond microcutter. The superconducting-transition temperature and the sample resistance were measured both before and after trimming the edges.