

*LATENT OPTICAL ANISOTROPY OF CUBIC CRYSTALS CONTAINING LOCAL CENTERS,
AND METHODS OF ITS STUDY**

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INTRODUCTION

THE idea that cubic crystals are isotropic in their optical properties, which is supported by all of experimental and theoretical crystal optics, is old and generally accepted. Whether pure or containing foreign activator impurities, cubic crystals possess neither dichroism of absorption nor birefringence, the characteristic manifestations of optical anisotropy, and thus optically resemble amorphous solids and liquids. However, in spite of the lack of direct manifestations of optical anisotropy, there are a number of interesting optical phenomena in which the so-called "latent" optical anisotropy of cubic crystals is manifested. The concept of latent anisotropy of completely isotropic optical media implies a transition from a macroscopic viewpoint of the optical properties to a microscopic one, taking into account the anisotropic properties of the elementary events of interaction of matter with light.

This review is concerned with the latent optical anisotropy of cubic crystals, due to the presence in the highly symmetric cubic structure of certain types of local defects, which we shall call anisotropic centers (AC). Their fundamental characteristic is their anisotropic structure, which commonly specifies a certain preferred direction or axis of the center (for sufficiently simple centers). Owing to the regularity of the cubic lattice, the axes of the AC cannot have

random directions. Rather, they are strictly oriented along the symmetry axes of some order or other in the crystal, i.e., the C_4 , C_3 , or C_2 axes existing in cubic crystals (Fig. 1). Owing to the presence of several equivalent axes, $3C_4$, $4C_3$, or $6C_2$, the AC of a certain type will form several equivalent groups (with $n = 3, 4$, or 6) in the crystal. These groups will differ only in their lattice orientation. Thus, a cubic crystal containing AC may be considered to be a macroscopically-isotropic superposition of several anisotropic crystals: three tetragonal, four trigonal, or six orthorhombic.

The anisotropic nature of the centers results in a marked anisotropy in the optical properties of the centers, such that each group of centers possessing parallel axes forms an optically-anisotropic system. The optical isotropy of the crystal is entirely due to the averaging of the anisotropic optical properties of the centers as a result of the existence of several groups of centers. Thus the optical anisotropy of the individual groups becomes latent. The existence of this latent anisotropy, however, gives rise to a number of peculiar optical phenomena in cubic crystals, distinguishing the latter from isotropic amorphous media. The study of these phenomena is not only of interest in itself, but is also of great importance in getting varied and valuable information on the AC, which are a very widespread type of defect in cubic crystals, often responsible for the most varied properties of the crystals.

In Sec. 1 we shall discuss various types of AC and their fundamental properties, and also indicate the

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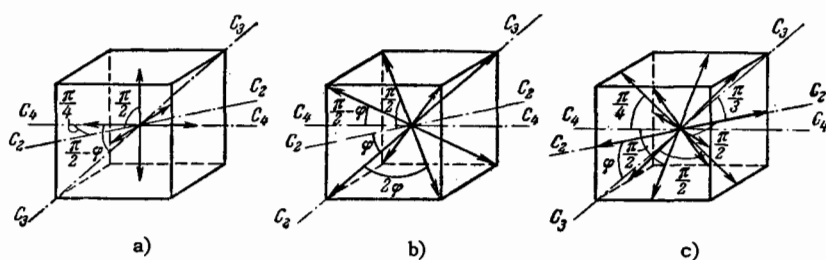


FIG. 1. Orientation of anisotropy centers in cubic crystals: a) along the C_4 axes; b) along the C_3 axes; c) along the C_2 axes.

physical phenomena in which the AC take part. The text of this section makes no pretense of completeness, having the goal of giving a general picture by concrete examples of the AC as a specific type of defect in cubic crystals. We shall especially discuss which optical properties of the AC are responsible for the optical anisotropy of cubic crystals, and the general principles of studying this anisotropy.

The following sections (2–5) are concerned with a review of studies on the individual characteristic optical phenomena involving the presence of AC in the structure, and with the information on the centers which we can get by studying these phenomena.

1. ANISOTROPIC CENTERS IN CUBIC CRYSTALS

a) Types of anisotropic centers and their structures. At present, the existence of many types of anisotropic defects has been established in cubic crystals. We shall be concerned with the “simplest” AC, in the structure of which we can distinguish one preferred direction, or with centers situated in a crystal field having a single preferred direction. We can consider the existence of a preferred direction, the axis of the center, to be a fundamental necessary and sufficient criterion defining the concept of the anisotropic center. The nature of the anisotropy of the centers may vary.

Above all, the anisotropy may be due to the complexity of the structure of the center itself, which may consist of several “point” defects, and thus extend over several atomic sites. A characteristic example of this type of AC is the well-known complex electron and hole color centers in alkali-halide crystals. In the model of the centers most widely used at present, that proposed by Seitz,^[1,2] these

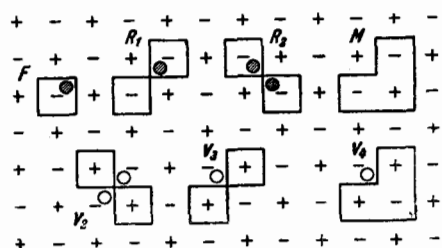


FIG. 2. Seitz's model for color centers in alkali-halide crystals.^[2] Squares = vacancies; shaded circles = electrons; open circles = holes.

centers are considered to be various complexes of cation and anion vacancies which have captured electrons or holes (Fig. 2). In this model, the R_1 and R_2 color centers are considered to be pairs of neighboring anion vacancies which have captured one or two electrons, respectively.* An M-center consists of the association of an F-center with a neutral pair of vacant sites. Seitz has proposed analogous models (based on cation vacancies and captured holes) for the V (hole) centers. As we see from the diagram, the AC of a given type may be compared with “diatomic” or “triatomic” molecules fixedly oriented in the structure. Figure 2 graphically demonstrates the basic distinction of the AC from “isotropic” centers (in this case F-centers). This consists in the existence of a definite axis in the AC, coinciding with the C_2 symmetry axis of the crystal in the cases of R- and M-centers. Figure 2 makes clear the reason for the “obligatory” fixed orientation of the AC with respect to the lattice.†

Complex color centers in alkali-halide crystals provide an example of the anisotropic combination of defects in a chemically-pure crystal. This type of AC also resembles in nature the complex impurity centers, e.g., as formed by association of two singly-charged impurity metal ions (Ag, Tl) replacing the cations of the ideal structure of the alkali-halide crystals. Figure 3 shows a center of paired Tl^+ ions produced in an x-irradiated CsI crystal, oriented along the C_4 axis.

Another type of structurally-complex AC consists of essentially heterogeneous point defects. In many cases, they are formed in ionic cubic crystals by isomorphous replacement of the ions of the ideal structure by impurity ions with differing valencies. Such a heterovalent replacement of ions in the crystal results in an excess electric charge which must be compensated by the existence in the structure of charged defects of the other kind. Thus, the incorporation into an ionic structure of impurity ions with differing charges leads to the enrichment in the crys-

* R_2 actually amounts to a pair of F-centers, and R_1 is the analogous singly-ionized pair. These centers are therefore often called F_2^- and $F_2^{\cdot-}$ centers.

† We must note that Seitz's models cannot be considered to be finally established as yet. There are also other models for the color centers, in particular those of Pick,^[2a] in which the complex electron centers are interpreted as associations of F-centers, and of Varley,^[2b] which involves interstitial atoms and ions.

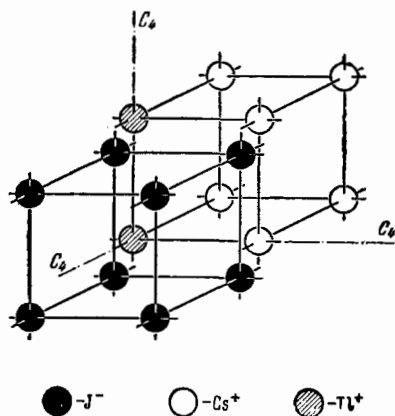


FIG. 3. Diagram of a center of paired Tl^+ ions in the CsI structure.

tal of "compensating" defects. Owing to the Coulomb attraction of these oppositely-charged various defects, they will tend to approach each other. Hence, the charge excess or deficit of the incorporated ion can be compensated by a corresponding defect in the immediate vicinity of the impurity ion, often in its first coordination sphere (the so-called principle of local compensation of charges^[2c]). The interaction of the impurity ion with neighboring compensating defects leads to the formation of complex "molecular" centers that exhibit anisotropy.

The variety of methods of compensation and types of compensating defects gives rise to many varied types of AC formed by the interaction of the impurity ions with defects. Thus, the excess positive charge of an incorporated cation may be compensated in several ways. Compensation by the formation of cation vacancies in the crystal structure occurs, for example, in the replacement of the singly-charged cations in alkali-halide crystals by the bivalent cations Ca^{++} , Sr^{++} , or Cd^{++} .^[3,4] In this case, the AC is oriented along the C_2 axis, belongs to the so-called class of Z-centers, and consists of a metal ion M^{++} with a neighboring cation vacancy. Its binding energy amounts to ~ 0.3 eV.^[4] Other types of combination of M^{++} with cation vacancies give other types of Z-centers.^[5] The compensation may also occur by introduction of a second foreign impurity having an excess negative charge into an anion site, or of an impurity having a positive charge deficit into a cation site. The latter occurs, for example,^[3] in the NiO crystal. Here, the structure consists of bivalent ions Ni^{++} and O^- , with some of the nickel ions trivalent. The charge of the Ni^{+3} can be compensated by an impurity of Li^+ ions in the cation sites (Fig. 4). Excess charges can be compensated by light charged particles (electrons) localized in the vicinity of the impurity ion.

We can consider analogously the means of compensation in other heterovalent replacements, i.e., introduction of cations with deficient positive charge, and

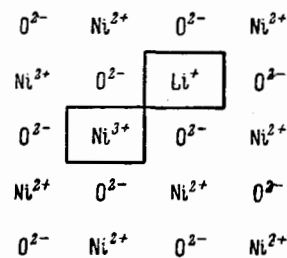


FIG. 4. Diagram of local charge compensation in nickel oxide.^[3]

the cases of deficient or excess negative charge in the introduction of anions into the structure (a characteristic example^[3] is the formation of associated complexes of S^{-2} ions and Br^- vacancies in the $AgBr$ system to which Ag_2S has been added).

In the case when the difference between the charges of the impurity ion and the ion which it replaces is large, several neighboring compensating defects may be required for complete local charge compensation of the impurity. Such a situation occurs, for example,^[6] in the alkali fluorides containing hexavalent uranium U^{+6} . Here the excess charge of +5 of the uranium in the cation site is compensated by five oxide ions O^{-2} replacing five of the six F^- ions in the first coordination sphere about the U^{+6} , with the formation of an AC oriented along the C_4 axis.

The examples given demonstrate the variety and widespread nature of the complex structures of the AC formed by heterovalent replacement in ionic crystals. Characteristic AC result from the incorporation into a cubic crystal of various sorts of anisotropic structures, molecules, radicals, or ionic complexes, which retain their internal bonding and individuality, and are held in the crystal structure in a fully definite manner. An example of these centers is the superoxide ion O_2^- in alkali halide crystals, in which the linear O_2^- ions are oriented along the $[110]$ axes.^[8a]

We have discussed above some examples of complex "structural" AC, consisting of several "point" defects, and forming sort of "quasimolecules" or molecules in the crystal structure. However, the anisotropy of the centers may involve not only complexity of structure, but also "positional anisotropy" of the center. In this case, a simple "point" center occurs in a structural site characterized by a lower non-cubic symmetry having a preferred direction, with resulting "orientation" of the center. Such a situation can occur, e.g., with interstitial atoms (Frenkel defects, atoms in excess of stoichiometry, or impurity atoms). The same situation can occur also for impurity atoms or vacancies located at sites possessing non-cubic local symmetry in a particular crystal structure. An example of such a cubic structure is given by cuprous oxide Cu_2O , in which the Cu ions occupy sites having the trigonal point symmetry D_{3d} . In all these cases, the simple "isotropic" center, on being put into the anisotropic

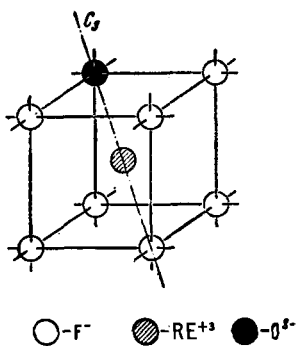


FIG. 5. A rare-earth ion in the fluorite structure.^[7]

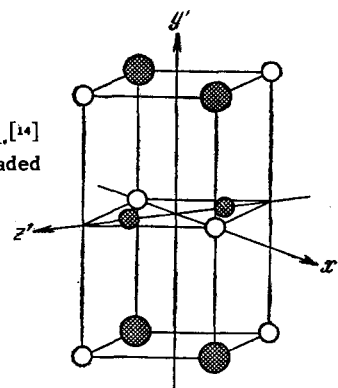
crystal field, is "oriented" by it in a direction determined by the symmetry of the field.

The anisotropy of the crystal field in which the center is located can arise not only in the cases discussed involving a regular structure, but also from some sort of defects which create asymmetry in the vicinity of a center which would be cubically-symmetric in the absence of the defects. Here the interaction of the impurity ions with their surroundings may not be strong enough to permit us to speak of the centers as structures of the molecular type, such as those discussed above. An example of such an orienting influence of defects is given by the system $\text{CaF}_2\text{-RE}^{+3}$, where the asymmetry of the field near the rare-earth ion RE^{+3} , orienting it along the C_3 axis, may arise from an O^{-2} ion replacing one of the eight F^- ions in the first coordination sphere to compensate the excess positive charge^[7] (Fig. 5).

It may seem that this case is completely analogous to the case mentioned above of activation of alkali fluorides by hexavalent uranium ions, in which the centers were treated as molecular structures. However, in the latter case the interaction of the ions with their surroundings is considerably stronger, and the spectra exhibit a marked electronic-vibrational character typical of molecular spectra. The rare-earth ions incorporated into the crystal structure interact considerably more weakly with it. Thus we have reason to consider them as centers whose orientation is determined by the symmetry of the field of the surrounding ions. Besides, a systematic classification is difficult here.

A peculiar "self-orientation" of "point" defects in cubic surroundings may also result from a particular effect of interaction of the electronic states of the centers with the motion of the ions of the surrounding structure, as discussed by Jahn and Teller.^[8] They formulated a principle applied to polyatomic molecules, which, as was shown subsequently in a number of papers,^[9-13] is of importance for local defects in crystals. The meaning of the Jahn-Teller principle as applied to point centers in cubic crystals is that, when the electronic levels of the center exhibit orbital degeneracy, the state in which the neighboring ions in the structure form a highly-symmetric cubic configuration becomes unstable.

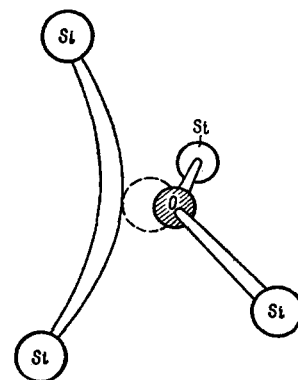
FIG. 6. Orientation of the molecule-ion Hal_2^- in the crystal.^[14] Open circles = alkali metal; shaded circles = halogen.



The ions surrounding the center are displaced to new equilibrium positions in such a way that they form a less symmetric geometric configuration about the center. As a result, the degeneracy of the levels of the center is at least partially relieved. Such a "self-consistent" local complex, consisting of a point center surrounded by a deformed coordination sphere, has a certain preferred direction, and constitutes an AC. The case which has been studied in greatest detail theoretically is that of octahedral coordination, as occurs, e.g., with a Tl^+ ion replacing a cation in alkali-halide crystals, or with F-centers in these crystals.^[11,8] Depending on the specific physical conditions, the distortion of the octahedron (of six halide ions) may be tetragonal or trigonal in symmetry, thus orienting the axis of the AC respectively along the C_4 or C_3 axis. For the triply-degenerate excited 3P_1 state of Tl^+ in KCl , the Jahn-Teller perturbation of the octahedron is tetragonal^[11] (the equilibrium symmetry of the octahedron of 6Cl^- is D_{4h}). Here the axis of the anisotropic complex is directed along the C_4 axis, and the level is split into two (singly- and doubly-) degenerate sublevels.

A highly interesting type of AC was recently discovered in alkali-halide crystals which had been x-irradiated at low temperatures.^[14] When an electron is removed from the electron-cloud of a halogen ion, the electron deficit (hole) produced is shared by two neighboring halide ions. Thus a peculiar molecular bond is formed between them and results in the approach of the ions. This center, which we may con-

FIG. 7. Model of an A-center in a silicon crystal.^[15] Dotted circle = silicon vacancy.



sider to be a negative molecule-ion Hal_2^- in the alkali-halide crystals, is oriented along the C_2 axis (Fig. 6). Thus, this AC, in distinction from all the others, is not due to any atomic defect in the structure, but is a particular form of self-capture of a hole, occurring largely through formation of a molecular linkage between the halide ions. This center is stable only at low temperatures.

In homopolar cubic crystals, the formation of AC may be due to the existence in the structure of anisotropic directed covalent bonds. A characteristic example of this are the so-called A-centers in irradiated silicon, in which vacancies have been created.^[15] An A-center (Fig. 7) is an oxygen atom in the site of a silicon-atom vacancy, where four broken bonds from the tetrahedron surrounding the Si atom vacancy will occur. The oxygen atom can accept two of these bonds, forming an anisotropic quasimolecule Si—O—Si. Depending on which pair of Si atoms is chosen for covalent binding to oxygen, six groups of such AC are possible, distinguished by their lattice orientation. It is interesting to note that the remaining bonds of two silicon atoms uncompensated by oxygen will form together an anisotropic Si—Si bridge, which in itself can act as an electron-capture center. The presence of directed covalent bonds may give rise to a large number of varied AC in the homopolar crystals of semiconductors containing impurities or defects.

As we see from the above discussion, many types of AC differing in nature exist in cubic crystals. This list of various types of centers could be extended. However, we can see even from the cited examples the great variety and the widespread nature of this type of defect in crystals. An essential point here is the fact that the AC occur among cubic crystals important in solid-state physics, such as the ionic alkali-halide crystals and the homopolar semiconductor crystals having the diamond or sphalerite structures.

We must not consider the AC to be completely stable entities, immovably fixed in the crystal. As with other types of defects, they can migrate through the crystal and participate in diffusion. Also, as is of greatest interest, they may change their lattice orientation in jumpwise fashion, and become distributed along several different equivalent directions or symmetry axes of the crystal. In this sense, the statistically probable lattice distribution of the AC over the $12/n$ directions of the C_n axes is dynamic in nature. The efficiency of the reorientation depends entirely on the concrete properties of the centers and the amount of activation energy required. In particular, certain types of complex centers, whose reorientation involves processes of low probability, e.g., interchange of positions of the heavy ions forming the center and its surroundings, may be considered to be quite stably fixed in the structure. On the other

hand, the reorientation of certain other AC may involve, for example, only a shift in the equilibrium positions in the configuration of the ions surrounding the center (Jahn-Teller AC) together with a change in the position of the electron compensating the excess charge, or with a rearrangement of bonds (A-centers in silicon); these AC may change their axial directions rather often. The requirement of a certain activation energy U to overcome the potential barrier between two energetically equivalent states leads to a strong temperature-dependence of the transition probability ω ($\omega \sim e^{-U/kT}$). We must also note that reorientation of the AC may occur not only directly, but by way of dissociation of complex centers and subsequent recombination to form a center having a different direction. The effect of processes of reorientation of AC on the optical properties involving the AC is obviously determined by the relation between the relaxation time for reorientation and the intrinsic time constant of the corresponding optical phenomenon. In many cases, effects involving reorientation of the centers have no influence, but in other cases they may be quite significant. We shall deal below with the problem of achieving a directed reorientation of the centers under defined external conditions, so as to bring about a preferred orientation of the centers along some one or a few axes.

In spite of the variety of types of AC, they all have one general property, which is essential in the specific optical phenomena involving the AC to be discussed. This property is the existence of one preferred direction in the structure of the complex centers or in the crystal field in which the point centers are situated. The existence of such a distinct axis of the centers is characteristic of the relatively "simple" centers, and in this case the axis of the center must necessarily coincide with one of the symmetry axes of the crystal, C_4 , C_3 , or C_2 . We must note that, in general, more complex centers are also possible (e.g., aggregated centers), having an irregular structure not permitting us to distinguish any single direction as a symmetry axis of order at least two. However, since very little is known about the properties of such centers, we shall not consider them, bearing in mind the possibility of generalizing the results for the "simple" AC to this case.

We shall consider from now on that the AC are rather simple entities having a single preferred axis oriented in the crystal along the [100], [110], or [111] directions, which correspondingly is a 4-, 2-, or 3-fold axis of the center. Obviously, the direction of the axis of the AC is its most important characteristic, directly involving the nature of the center itself. At the same time, we must note that sometimes an ambiguity arises in the construction of models for the AC, even when their orientation is known. In a

final selection of a model for the center in this case, we must bring in further considerations (this may be seen easily from Fig. 2, in which one and the same direction C_2 is the orientation axis of color centers of various types: R_1 , R_2 , and M).

The AC are not only very widespread in cubic crystals, but are also an important type of defect participating in many phenomena in crystals. In particular, complex structural centers exhibiting anisotropy are commonly the first stage in various processes involving aggregation of atomic particles in crystals into larger particles. For example, these include chemical reactions in solids and the separation of new phases within the crystal structure;^[3] various phenomena of coagulation of atoms and formation of colloidal particles in crystals; photochemical decomposition of crystals and the phenomena taking place in the various stages of the photographic process,^[16] etc. The complex centers involving vacancies exert an appreciable influence on the ionic conductivity of crystals.^[4] Characteristic phenomena due to the presence of AC are observed in the study of the dielectric properties of ionic crystals.^[17] These phenomena involve AC consisting of "charged" point defects and not possessing centers of inversion, thus manifesting a permanent dipole moment (e.g., a neutral pair of oppositely-charged vacancies in alkali-halide crystals). The direction of the dipole moment may change in an external electromagnetic field by reorientation of the center by jumpwise transition, e.g., of a charged vacancy into a neighboring site. This process will have a characteristic effect on the dielectric-loss properties of the crystals.^[17] Finally, we must mention the participation of the local levels of the AC in semiconduction processes. Here the AC may act as donor and acceptor centers, or as capture and recombination centers. Also, the AC may act as emission and capture centers in luminescent processes in crystal phosphors. The role of AC as sources of local levels shows no specific characteristics in these processes, as compared with the role of other defects. However, it is important to note here how widespread the AC are among the local centers responsible for the semiconducting and luminescent properties of crystals. In this regard, the evolution of the theory of luminescence centers in activated alkali-halide crystals is indicative; this development has led to the conclusion that an important role is played in luminescence, not only by the simple single activator ions, but also by more complex centers produced by the interaction of the activator ions with each other or with lattice defects.^[18]

b) Optical properties of the anisotropic centers. The existence of AC in cubic crystals often determines their optical properties. Transitions between the levels of the AC give rise to additional absorption bands, in particular, in the transparent spectral re-

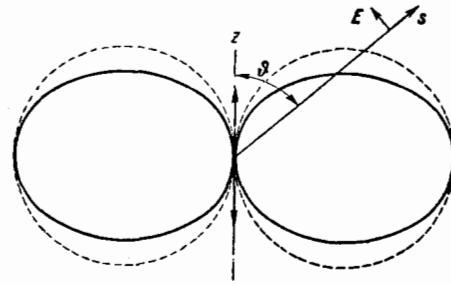


FIG. 8. Emission field of an electric linear dipole. Dotted curve = amplitude; solid curve = intensity.

gions of the crystals. They also give rise to luminescence. They may also make a definite contribution to the refractive dispersion of crystals. Above all, the specific character of the optical properties of cubic crystals containing AC is due to the peculiarities of the optical properties of the individual AC. As has been noted above, the most characteristic property of the AC is the fact that the elementary emission (or absorption) appearing in the optical transitions between the levels of the individual centers is markedly anisotropic in its spatial distribution. The existence of this optical microanisotropy of the individual AC is a consequence of the most general properties of the matrix elements of the transition, which describe the probabilities of the optical transitions between levels in the quantum theory of emission. Since these properties essentially determine the major peculiarities of the phenomena being discussed, we must mention here the fundamental concepts of this subject (see also ^[19]).

The matrix element of the dipole moment for a transition between the energy states a and b has the form

$$P^{ab} = \int \Psi_a \mathbf{P} \Psi_b d\tau = -e \int \Psi_a \mathbf{r} \Psi_b d\tau, \quad (1.1)$$

where $\mathbf{P} = e\mathbf{r}$ is the dipole moment, and Ψ_a and Ψ_b are the wave functions of the states between which the transition occurs.

The components of the matrix element may be written as

$$P_x = -e \int \Psi_a x \Psi_b d\tau, \quad P_y = -e \int \Psi_a y \Psi_b d\tau,$$

$$P_z = -e \int \Psi_a z \Psi_b d\tau.$$

The emission associated with each of these components of the matrix dipole moment is linearly polarized, and is anisotropic in its spatial distribution. The spatial distribution of the emission (or absorption) corresponding to a single component of the matrix element of the dipole moment, e.g., P_z , is equivalent to the emission from a linear harmonic oscillator directed along the z axis (Fig. 8). The light emitted by the oscillator is completely polarized in the meridional plane, and the spatial distribution is axially symmetric. For a direction forming an angle

θ with the z axis of the oscillator, the flux density of electromagnetic energy is

$$I(\theta) = \frac{\omega^4 P^2}{4\pi r_0^2 c^3} \sin^2 \theta, \quad (1.2)$$

where ω is the frequency of the light, P is the amplitude of the oscillating dipole moment, r_0 is the distance from the dipole, and c is the speed of light.

The emission is maximum in a direction normal to the axis of the dipole, and vanishes when observed along the axis of oscillation. This oscillator, which is known as a Hertz dipole, is the simplest and most important classical model for a quantum emitter corresponding to a single component of the matrix element of the dipole moment (a π_e -oscillator).

For systems having a definite direction, such as the AC, a matrix element of the following type is also of great importance:

$$P_{x \pm iy} = -e \int \Psi_a(x \pm iy) \Psi_b d\tau. \quad (1.3)$$

In its spatial distribution of emission, this element corresponds to a classical model consisting of two mutually-perpendicular coherent Hertz dipoles in the xy plane, performing oscillations with a phase difference of $\pm \pi/2$ (an electric rotator, Fig. 9). The spatial distribution of the emission has the form:

$$I_{\parallel}(\theta) = \frac{\omega^4 P^2}{4\pi r_0^2 c^3} \cos^2 \theta, \quad I_{\perp}(\theta) = \frac{\omega^4 P^2}{4\pi r_0^2 c^3}, \quad (1.4)$$

where $I_{\parallel}(\theta)$ and $I_{\perp}(\theta)$ are the components of the energy flux having oscillation of the electric vector \mathbf{E} in the meridional plane and normal to it, respectively. The emission is maximum in the direction of the axis of the rotator, where it is circularly polarized, and minimum in a direction in the plane of the rotator, where it is linearly polarized in this plane. In the general case, the emission is elliptically polarized. The planar electric rotator is a model for the properties of the electromagnetic field of the important quantum emitter corresponding to the matrix element of Eq. (1.3), or the so-called σ_e -oscillator.

Besides the electric-dipole transitions, there are also transitions of higher multipole type, among which the most important are the magnetic-dipole transitions. The matrix element of a magnetic-dipole transition is

$$M^{ab} = \int \Psi_a \mathbf{M} \Psi_b d\tau, \quad (1.5)$$

where \mathbf{M} is the magnetic-moment operator. Complete analogy exists between the spatial distribution of the emission for the components of the matrix elements of magnetic-dipole transitions M_x, M_y, M_z and the corresponding components P_x, P_y, P_z of electric-dipole transitions, as well as between elements of the types M_{x+iy} and P_{x+iy} . As in the case of electric transitions, the spatial distribution for magnetic quantum emitters may be represented by the models of classical magnetic linear (π_m) and planar (σ_m) oscillators, whose spatial distribution of emission is

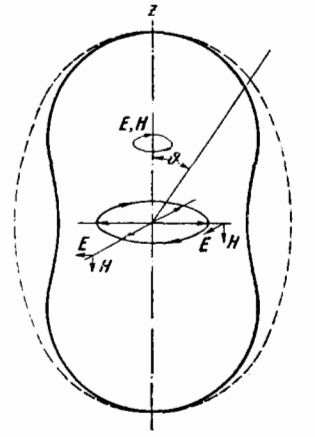


FIG. 9. Emission field of an electric rotator.

completely analogous to that of the π_e - and σ_e -oscillators, respectively, with interchange of roles of the \mathbf{E} and \mathbf{H} vectors of the electromagnetic field.

The anisotropy of the optical properties of quantum emitters corresponding to the components of the matrix elements of dipole transitions is highly significant, since in an elementary transition between two non-degenerate states, the components of the matrix elements are generally unequal. Consequently, elementary emission is always anisotropic and polarized. A typical example is given by free atoms, for which the selection rules for the magnetic quantum number M permit only π -transitions for $\Delta M = 0$ ($P_z \neq 0$ or $M_z \neq 0$), while for $\Delta M = \pm 1$, they permit only σ -transitions ($P_{x+iy} \neq 0$ or $M_{x+iy} \neq 0$).

Anisotropy of emission in a transition between two levels may not be manifested, or may be only partial, if the levels are degenerate and the transition is a superposition, e.g., of π - and σ -transitions. Hence, a low multiplicity of degeneracy of the levels of a system is an important condition for the existence of anisotropic optical properties in the transitions between the levels. This condition is generally satisfied by the AC, for which the degeneracy of the levels is low, owing to the lowered symmetry. Hence, we can consider the general reasons for the optical anisotropy of the AC to be, on the one hand, the anisotropic properties of elementary quantum transitions, and on the other hand, the low degree of degeneracy of the levels, associated with the low symmetry of the centers.

This conclusion can be illustrated by the example of a special case of the AC, for which a rigorous theoretical treatment can be made. This AC is an impurity atom retaining its individual character in a crystal field possessing a single symmetry axis C_n ($n = 2, 3, \text{ or } 4$). As is known (see, e.g., [20]), in a crystal field the $(2J+1)$ -fold degenerate levels of the free atom are split in a manner determined by the symmetry of the field. The states of the split levels may be characterized by the so-called crystal quantum number μ , which is in a certain sense analogous to the magnetic quantum number M , in defining the

"quasimoment" with respect to the axis. These states may be non-degenerate ($A_{|\mu|}$), or doubly degenerate ($E_{|\mu|}^{\prime}$). For the split levels of an atom having an even number of electrons ($J = \text{integer}$), the possible states are non-degenerate (A_0, A_1, A_2) and doubly degenerate states (E_1^{\prime}), while for an atom with an odd number of electrons ($J = \text{half-integer}$), they are doubly-degenerate states ($E_{1/2}^{\prime}$ and $E_{3/2}^{\prime}$). When there is a rotation symmetry axis C_n of finite order n , the strict selection rule is the rule for the quantum number μ . For electric and magnetic dipole transitions, this rule permits transitions having $|\Delta\mu| \leq 1$. Here if we align the z axis of the Cartesian coordinate system with the direction of C_n , the following selection rules hold for the components of the matrix elements, arising from the symmetry of the corresponding Ψ -functions:

$$\left. \begin{aligned} P_z &\neq 0 && \text{when } \Delta\mu = 0, \\ P_x \pm iy &\neq 0 && \text{when } \Delta\mu = \pm 1, \\ M_z &\neq 0 && \text{when } \Delta\mu = 0, \\ M_x \pm iy &\neq 0 && \text{when } \Delta\mu = \pm 1. \end{aligned} \right\} \quad (1.6)$$

Thus, depending on the value of $\Delta\mu$, the individual optical transitions between levels having certain values of μ will correspond to π_e^- , σ_e^- , π_m^- , or σ_m^- oscillators oriented along the symmetry axes of the centers.*

For the complex "polyatomic" AC, the problem of the polarization of the transitions also may be reduced to that of the symmetry properties of the wave functions of the centers entering into the expression for the matrix element of the transition [Eq. (1.1)]. For certain of these AC, mainly the color centers in alkali-halide crystals, concrete theoretical calculations have been made. Thus, Vinetskii and Deïgen^[21] have made a quantum-mechanical study, using the macroscopic approximation, of the $F_2(R_2)$ - and $F_2^+(R_1)$ -centers (see Fig. 2). In this approximation, these centers are analogous to the hydrogen molecule and molecule-ion. They showed that the optical transitions to the first two excited states of the centers are polarized. The polarization exhibits axial symmetry about the axis of the centers, which coincides with the C_2 axis of the crystal, and the absorption of polarized light varies as $\cos^2\theta$ and $\sin^2\theta$, respectively, for the two transitions. Here, θ is the angle between the electric vector \mathbf{E} of the light and the axis of the centers. These relations are equivalent [see Eqs. (1.3) and (1.4)] to the light absorption of completely anisotropic plane (σ_e) and linear (π_e) oscillators oriented along the axis of the centers. Gourary and Luke^[22] have studied the levels of the M-center. They used the approximation of a crystal

*We might point out an exception in the case of the transition between the doubly-degenerate states $E_{1/2}^{\prime} \rightarrow E_{3/2}^{\prime}$, for which the anisotropy vanishes owing to the superposition of π - and σ -transitions.

structure of point ions, and assumed the Seitz model of triple vacancies (two negative and one positive) having a captured electron (Fig. 2). A calculation of the ground state and the two lowest excited states of an M-center possessing C_{2v} symmetry showed that the transition to the lowest excited state corresponds to a dipole moment in the [110] direction joining the two negative vacancies,^[23] while the transition to the upper excited state corresponds to a moment oriented along the [100] direction normal to the plane in which the center lies. In^[24], in which the M-centers were studied in the macroscopic approximation, a different result was obtained: the transitions to the two lowest excited states correspond to partially anisotropic oscillators, the degree of anisotropy depending on the concrete parameters of the centers.

Thus, there is still no rigorous theoretical treatment of the properties of the optical transitions in a general form for the AC (it could be carried out on the basis of group theory). Nevertheless, the conceptions presented above, and the results of theoretical calculations for several special cases of the AC, as well as numerous experimental results to be given below, definitely indicate that the individual AC are also anisotropic in the optical sense.

In order to describe this anisotropy, it is very convenient to use the classical model, which has proved to be justified in many cases, and with regard to optical properties, to treat the AC as dipole-type anisotropic oscillators (electric or magnetic) of various "forms" (linear, planar) in fixed orientation along the axis of the centers.

The nature (multipole type) of such an oscillator is a very important characteristic of the AC, since it permits us to determine the quantum properties of the levels of the center involved in the transition, and it gives us information essential in interpreting the energy diagram of the center.

c) Latent optical anisotropy of cubic crystals containing anisotropic centers and general principles of study. In general, several equivalent groups of centers are oriented in the cubic crystal along the several C_n axes of the same order; the number of such groups is $12/n$, but if the AC do not possess inversion centers, the number of groups is $24/n$. Owing to the existence of these groups and the statistical uniform distribution of the centers among them, the optical microanisotropy of the centers is completely averaged out in the macroscopic optical properties of the crystal. (The existence of such an averaging may be directly verified by summing the intensity of the electromagnetic emission field, as given by Eqs. (1.3) and (1.4), of three mutually-perpendicular π - or σ -oscillators corresponding to AC directed along the three C_4 axes, or of four oscillators directed along the four C_3 axes, or of six oscillators directed along the six C_2 axes.) This statistical averaging, as was stated in the Introduction, causes the optical anisotropy of cubic crystals contain-

ing anisotropic centers to become latent. In particular, the crystal will not exhibit dichroic absorption. The spectral regions in which latent anisotropy of optical absorption (or emission) of cubic crystals will occur will obviously be limited to the spectral regions of absorption and emission of the AC. The region of latent optical anisotropy is extended when we take into account the contribution of the AC to the dispersion, since the refractive index also exhibits latent anisotropy owing to the anisotropy of the high-frequency polarizability of the individual centers.*

In order to reveal the latent anisotropy of cubic crystals, we must study their optical properties under some directional external influence. If this influence is of such a type that the resulting effect is unambiguously related to the relative orientations of the direction of the external influence and the symmetry axes of the centers, then in general, this effect will differ for different groups of centers. The degree of participation of the individual groups of centers and the size of the effect for each group will obviously vary as we vary the relative orientations of the direction of the external influence, the direction of observation, and the symmetry axes of the crystal. The pattern of a phenomenon observed under certain fixed experimental conditions will be a superposition of the patterns given by the individual groups of centers. By varying these conditions and analyzing the changes in the observed pattern, we can get an idea both of the distribution of the centers within the crystal and of their properties. This principle is the basis of all the existing methods of detecting and studying the latent optical anisotropy of cubic crystals containing AC.

One possible directional action is that of light, which is anisotropic, even if unpolarized, owing to the existence of a distinct direction, that of the light ray. The light absorbed by the crystal may bring about, on the one hand, photochemical breakdown and transformation of the centers, or on the other hand, luminescence. Observation of both effects may be used to reveal latent anisotropy. We can also apply an anisotropic external influence by creating elastic strains in the crystal by uniaxial tension or compression, resulting in shift and splitting of the lines in the absorption and emission spectra. Observation of the optical phenomena which

*We must take note that the conclusion that cubic crystals are optically isotropic is valid only in the approximation neglecting spatial dispersion, i. e., the dependence of the complex refractive index not only on the frequency ω of the light but also on its wavelength λ . If we take into account the spatial dispersion, optical anisotropy of cubic crystals then becomes theoretically possible, with its characteristic manifestations [birefringence^[25,26] and anisotropic absorption (quadrupole transitions^[27])]. These effects of "overt" optical anisotropy must theoretically be especially strong in the region of exciton absorption,^[28] where they have been observed experimentally.^[29] However, this entire set of problems is outside the limits of this review, which is concerned with "ordinary" crystal optics, neglecting spatial-dispersion effects.

appear upon applying homogeneous or magnetic fields to the crystal may also be used as means of revealing latent optical anisotropy. In the following sections, all of these methods will be discussed in more detail.

As we shall see, the ways of revealing the latent optical anisotropy give us valuable information on the symmetry properties of the centers and on the elementary-oscillator type of the centers. Data on the symmetry of the centers and their lattice orientation are often a rigorous criterion of the correctness of some particular model of the center, and they may indicate ways to construct models. A knowledge of the elementary-oscillator type is necessary in the interpretation of the energy-level diagram of the center. Besides this direct information on the properties of the centers, study of latent anisotropy provides information in a number of cases on the complex interactions between various centers in crystals.

2. PHOTOCHEMICAL PROCESSES IN CUBIC CRYSTALS CONTAINING ANISOTROPIC CENTERS

The existence of AC capable of being destroyed or transformed by light is involved in the appearance of optical anisotropy in cubic crystals upon illumination by photochemically-active polarized light. The appearance of dichroism when color centers are disrupted photochemically in x-irradiated NaCl and KCl crystals was first discovered by Nikitin^[29a] in 1943. However, it seems that Nikitin did not note that the magnitude of the resulting dichroism depends on the relative orientations of the plane of polarization of the light and the symmetry axes of the crystal. A simple study shows that such a relation must exist, since the relative degree to which the separate groups of centers participate in the light absorption leading to the photochemical processes is determined by the orientation of the acting light vector with respect to the axes of the anisotropic centers, and thus, to the crystal axes. Hence, the magnitude of the observed effect is similarly determined. The anisotropy of photochemical transformations in cubic crystals containing AC may be very marked, since when the centers are oriented in a relatively small number of crystallographic directions, we may select a direction of the effective vector of the photochemically-active light such that centers having certain definite orientations preferentially absorb the light and are affected. Study of anisotropic photochemical transformations of centers with definite polarization directions of the photochemically-active light permits us to determine the lattice orientation of the absorbing dipoles, and hence, of the AC as well as the dipole type.

Ueta^[30] was the first to consider the dependence of the induced dichroism on the orientation of the crystal and the possibility of using this phenomenon to study the anisotropic properties of the centers. This

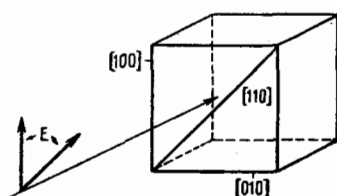


FIG. 10. Diagram of the orientation of the crystal axes and the electric vector E of the light in experiments on anisotropic bleaching of crystals.

subject was taken up somewhat later independently by Feofilov.^[31]

The inhomogeneity created in the distribution of the AC with respect to the crystal axes by photochemically-active polarized light can be studied by various optical methods. The most direct method is to study the dichroism in the absorption bands of the AC due to the disturbance of the homogeneous axial distribution of the AC.^[30] Study of such an anisotropic bleaching of the bands is possible when the concentration of centers is sufficiently high, so as to ensure measurable values of the absorption coefficients. Inhomogeneous distribution may also be studied by way of the changes which it produces in the characteristics of the polarized luminescence of the crystals.^[31] A very sensitive method for detecting inhomogeneous distribution of centers is the study of the flash of recombination luminescence of an excited phosphor when it is stimulated by polarized light in the spectral region of the AC bands. Here the AC serve as capture centers for electrons or holes.^[32] In this case, the intensity of the flash upon illumination by polarized light is proportional to the corresponding polarized absorption coefficient in the AC bands, which may be too small to be measured directly. Finally, in case that the AC are emission centers, inhomogeneous distribution with respect to the axes may lead to the appearance of polarized phosphorescence of crystals.^[33]

Disruption of AC by light ordinarily exhibits a "photothermal" character, in which a center brought by light absorption into an excited state is dissociated by thermal activation. Here the disruption of the center may involve either electronic or ionic processes, or others. In the former case, e.g., photothermal ionization of a center takes place, so that the center loses its optical electron and ceases to be optically effective. In the latter case, the excitation of

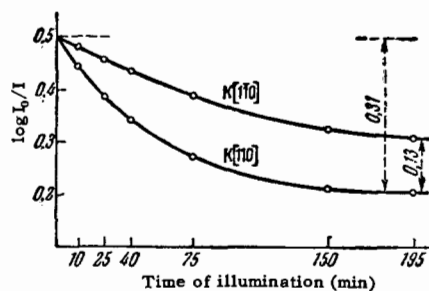


FIG. 11. Relation of the absorption coefficient K at the maximum of the M-band of KCl to the time of illumination of the crystal by light polarized \parallel [110].^[30]

the center may facilitate dissociation due to diffusion of the defects constituting the AC. Here, while the polarized light disrupts preferentially the AC having a certain orientation, but acts considerably more weakly on centers of other orientations, the disrupted AC can often be recreated (or recombine) in all possible orientations. Thus, a process occurs involving disruption of AC of a certain orientation by the polarized light, usually accompanied by enrichment in the other orientations. This process shows a complex dynamic character, and depends on the concentration and properties of the AC, on the time and external factors such as the intensity of the acting polarized light, and especially the temperature. We must note that the action of light may bring about not only the disruption of the AC, but also a simple reorientation due to a reduction of the activation energy for jump transitions in the excited state. This process, in which the total number of AC remains constant, in distinction from the disruption process, also results in an inhomogeneous axial distribution of the AC. Here, as in the disruption of the centers, reverse processes exist in which the centers reoriented by the light revert to their original state. This prevents the complete orientation of the AC in a single lattice direction. The complexity of the microprocesses brought about by photochemically-active light complicates the construction of a quantitative theory of the phenomenon. However, as is shown by calculation, qualitative studies of the characteristics of anisotropic transforma-

Table I

Orientation axis of the optical dipole of the center	Bleaching by light polarized along [100], with absorption measured with polarization parallel to		Bleaching by light polarized along [110], with absorption measured with polarization parallel to	
	[100]	[010]	[110]	[110]
[100]	K_{100} decreases	K_{010} does not decrease	$\Delta K_{110} = \Delta K_{110}$	
[110]	Initial rate of decrease of K_{100} is twice that of K_{010}		Initial rate of decrease of K_{110} is five times that of K_{110}	
[111]	$\Delta K_{100} = \Delta K_{010}$		K_{110} decreases	K_{110} does not decrease

K = the absorption coefficient for polarization direction of the light given by the subscript. ΔK = magnitude of change in the absorption coefficient.

tions of the AC under the action of polarized light are quite sufficient to obtain reliable information on their lattice orientation and the type of the absorbing dipoles.

Most of the studies of anisotropic photochemical transformations of AC in cubic crystals have involved color centers in alkali and alkali-earth halides, and have been performed by studying induced dichroism of the absorption bands of the AC. The commonly-used experimental setup has the following form (Fig. 10). A crystal cleaved along cube faces is illuminated with polarized photochemically-active light in an AC band. The light is incident normal to the (001) face of the crystal. The photochemically-active light is polarized with the electric vector \mathbf{E} along [100] or [110]. After one has illuminated the crystal with the photochemically-active light, one measures the absorption coefficient of the light (in the same or any other AC band) with the same incident direction. In the former case, the polarization is taken with $\mathbf{E} \parallel [100]$ and $\mathbf{E} \parallel [010]$; and in the latter case, with $\mathbf{E} \parallel [110]$ and $\mathbf{E} \parallel [1\bar{1}0]$ (i.e., with polarization coincident with or normal to the bleaching light). The comparison of the absorption coefficients in polarized light among themselves and with the isotropic absorption coefficient existing before bleaching permits us to determine the lattice orientation of the effective dipoles. Table I, taken from a study by Compton and Klick,^[34] gives such an "index" for the case of linear effective dipoles parallel to the axes of the AC (reorientation of the centers being neglected). Analogous tables can be compiled without difficulty for other multipoles and their combinations, as describing, on the one hand, transitions in centers leading to their disruption, and on the other hand, transitions in the regions where the observation of dichroism is carried out.

The greatest number of experimental studies has been concerned with electron color centers in alkali-halide crystals (R-, M-, N-, and O-centers), which give rise to the absorption bands on the long-wavelength side of the F-band. Especially detailed study has been made of the phenomenon of anisotropic transformation of M-centers in KCl, which was discovered in the study of Ueta.^[30] He subjected an additively-colored KCl crystal to prolonged illumination with light in the region of the M-band. The light was polarized along one of the twofold axes lying in the plane of the plate, which had been cleaved from the crystal parallel to (100). He observed the appearance of dichroism (Fig. 11), the analysis of which showed that the anisotropic centers responsible for the M-band are oriented along the C_2 axes.

In later studies, Ishii, Tomiki, and Ueta^[35] demonstrated the strong effect of temperature on the anisotropic transformation of the M-centers upon illumination with light in the M-band. In particular, they showed that at high temperatures ($\sim 100^\circ\text{C}$), the anisotropic effects completely vanish. This indicates that ionic processes play a role in reorientation phe-

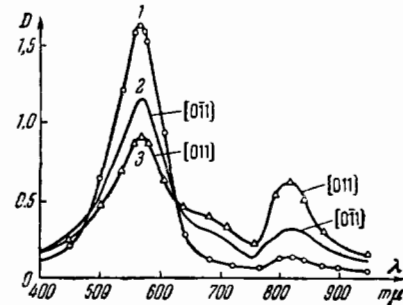


FIG. 12. Dichroism in the region of the F- and M-absorption bands in KCl produced by illumination by light in the F-band polarized along [011].^[41] 1 - before illumination; 2, 3 - after illumination.

nomena of the centers. These authors^[35] also demonstrated the phenomenon of thermal reorientation of M-centers in the ground state with an activation energy of ~ 1 eV. The studies of van Doorn and Haven^[37,38] dealt with anisotropic photochemical transformations of M-centers in KCl at low temperatures ($T = 77^\circ\text{K}$). They showed that dichroism of the M-bands is not produced at this temperature by polarized illumination in the M-band.

Shmit^[36] and van Doorn and Haven^[37] have obtained very interesting results by studying photochemical transformations in KCl crystals containing F- and M-centers when illuminated by polarized light in the region of the F-band. Here dichroism appeared not only in the absorption region of the M-centers being produced, but also in the region of the F-centers being bleached. The dichroism in the F- and M-bands exhibited opposite signs (Fig. 12). It is very interesting that dichroism appeared in the F-band, which is generally considered to involve completely isotropic centers.

A number of studies^[37,38] have attempted to explain this phenomenon by assuming that the M-centers possess two absorption bands, one of which is the "ordinary" M-band, situated on the long-wavelength side of the F-band, and the other overlapping the F-band [the F(M)-band]. Transitions to these two excited states are polarized parallel and perpendicular to the axis of the center, thus explaining the opposite signs of the induced dichroism of the M- and F(M)-bands. Van Doorn^[37,38] ascribed the appearance of dichroism upon polarized illumination in the F-band to reorientation of the M-centers by ion migration upon excitation in the F(M)-band.

This interesting phenomenon in complex electron color centers has been subsequently investigated in detail in a number of studies. Kuwabara and Misu^[39] demonstrated that the "linked" dichroism of opposite sign in the F- and M-bands in KCl also appears upon illumination with polarized light in the M-band at room temperature. The authors determined the ratio of the oscillator strengths for the two bands of the M-centers [M and F(M)]. This ratio turned out to be $f_{F(M)}/f_M = 0.82$, and by comparison with theory they

found that the symmetry of the centers is D_{2h} . On the basis of a comparison of the type of dichroism of the M- and F(M)-bands induced by illumination in the M-band at 20°C and in the F-band at 77°K, these authors^[39] proposed that the mechanism of appearance of dichroism differs in these two cases. In the former case, centers having a certain orientation become ionized, and thereupon part of the electrons are captured by centers of differing orientations. In the latter case, reorientation of centers in the excited state takes place by jump transition of vacancies, with conservation of the total number of centers. In a subsequent study, Kuwabara and Misu^[40] showed that the dichroism of the bands of the complex centers (M, R, and N) induced by illumination in the F-band depends on the region of the F-band in which the illumination is carried out. On the basis of this observation, these authors concluded that the F-band is complex in nature, various regions overlapping with the bands of various complex color centers. Okamoto^[40a] came to an analogous conclusion based on a detailed study of photochemical bleaching of color centers in KCl. He discovered several additional bands, which he ascribed to different excited states of M-centers, and determined the type of the absorbing dipoles for these bands.

However, we cannot consider the interpretation of the phenomenon as being due to the overlapping of the spectral bands of different centers to be conclusively proved. A number of observations favor the assumption that the anisotropic action of polarized light in the region of one spectral band on another band involves the interaction of centers of different types and the transfer of energy among them.

Yanson and Shmit^[41] showed an interconnection between dichroism in the F- and M-bands, and advanced the hypothesis that the dichroism of the F-band involves the effect of oriented M-centers, whose dipole field gives rise to an electric polarization of definite direction throughout the crystal, including the F-centers.

Kanzaki^[42] has made a detailed study of the "dichroism spectra" (spectral characteristics of the degree of dichroism) in the region of the F- and M-bands in KCl and of the form of these bands as functions of the time of illumination at $T = 77^\circ\text{K}$ by polarized light in the F-band. He showed that the dichroic effect depends essentially on the concentration of F- and M-centers, and that during low-temperature illumination in the F-band, no change takes place in the total number of M-centers. This author analyzed the mechanism of reorientation of the M-centers upon illumination in the F-band, and concluded on the basis of his experimental results that this reorientation does not involve direct absorption of F-quanta by the M-centers, but is due to energy transfer between the F- and M-centers. Here the polarization effects in the absorption of the F-centers were explained by the anisotropic influence of nearby M-centers on the F-

centers, as was suggested in the studies of Yanson and Shmit^[41] and Lambe and Compton.^[55]

Thus, studies of anisotropic transformations of the M-centers have firmly established their anisotropic character and their orientation along the twofold symmetry axes, as well as the linear nature of the dipoles of the M-band and a number of other properties of the M-centers. They have also shown a close interaction between the different bands, which, however, still requires further study to elucidate its nature.

Certain studies have been concerned with anisotropic transformations of other electron color centers in ionic crystals although not in detail as was the case for the M-centers. Feofilov^[31] applied the measurement of polarized luminescence to study induced dichroism and thus studied photochemical transformations of complex color centers in NaF and CaF_2 crystals. The results of this study confirmed the data obtained earlier by the method of azimuthal dependence of the polarization of luminescence (see below, Sec. 3) on the anisotropy of the centers and their orientations. The orientations were along the C_2 and C_4 axes, respectively, in concordance with the model for the $F_2(R_2)$ -centers. The study of anisotropic photochemical transformations of complex color centers in this research permitted the author to choose unequivocally between the two possible oscillator models for these centers, which were equally successful in describing the azimuthal and spectral dependences of the degree of polarization of the luminescence.

Shatalov^[43] has studied the anisotropy of the color centers arising during photochemical action on F-centers in heated alkali-halide crystals, and demonstrated that they are oriented along the C_2 axes, in agreement with the author's suggestion that the objects studied had the structure of F_2 -centers.

Some Japanese authors have observed dichroism in the R-bands in KCl^[35] and LiF.^[44] In the latter case, the dichroism appeared upon illumination of the crystals by polarized light having $E \parallel [110]$. Photochemically-active light polarized along $[100]$ did not produce dichroism. Hence the authors concluded that the centers involved were oriented along the $[111]$ axes of the crystal. The smallness of the dichroism indicated the low degree of anisotropy of the absorbing oscillators. Okamoto^[40a] also concluded that the R-centers in KCl are oriented along $[111]$.

Khellenurme^[32] discovered anisotropy in the complex N- and O-color centers in KCl, which exhibit bands in the infra-red region of the spectrum, and are commonly considered to be rather large aggregates of defects. The anisotropy was observed in the emission flash of Tl^+ in the visible region (the KCl crystal being activated with Tl^+) upon illumination in the N-, O-, and other bands as well, in which the corresponding centers played the role of electron-capture centers. When the crystal had been subjected to preliminary illumination by light in the region of various absorption

bands, polarized along [110], the intensity of the flash of visible light was found to vary with the polarization of the emitted light. This "dichroic" effect in the flash, involving inhomogeneous distribution of the AC existing after the polarized illumination, was observed upon illumination in the F-, M-, N-, and O-bands. Here the dichroism appeared not only in the band of the photoactive illumination, but also in all the other bands, indicating an interaction between the centers of various types. This phenomenon was also observed in [40a], in which the M_1 -centers were shown to be oriented along [110] and the N_2 -centers along [111].

Nishimaki, Kojima, and Kojima [45a] and Lüty [45b] have studied anisotropic photochemical transformations in the so-called A- and B-bands, which appear at the edges of the F-band upon illumination of additively-colored KCl by light in the F-band. The authors [45a, 45b] established a relation between these bands and transitions in a single center (the A-center) oriented along [110]. On the basis of this conclusion, as well as of the results of study of bands in KCl containing an NaCl impurity, the authors suggested a model for the A-center as being an F-center in whose vicinity one of the six nearest K^+ ions has been replaced by Na^+ .

A number of studies have been concerned with bleaching by polarized light of the V (hole) bands in alkali-halide crystals. The appearance of these studies was stimulated by the discovery by paramagnetic resonance [14] of certain anisotropic centers oriented along [110] in the series of alkali-halide crystals. These centers were formed by x-irradiation of the crystals at low temperatures, i.e., under conditions in which a V_1 (hole) absorption band ordinarily appears. Lambe and West [45] showed that anisotropic photochemical transformations do not occur in the V_1 -band, in concordance with the model of Seitz, who considered V_1 -centers to be the hole analog of F-centers.* This permitted them to conclude that the V_1 -center is not the AC responsible for the observed EPR signal of the irradiated crystals. Känzig and his associates [14] later showed that these AC are self-captured holes or "molecule-ions" F_2^- , Cl_2^- , Br_2^- , I_2^- , oriented along [110] (see Sec. 1 of this review). Delbecq, Smaller, and Yuster [46] have discovered absorption bands exhibiting anisotropic bleaching in polarized light in KCl crystals irradiated at low temperatures (pure or containing impurities). Studies of the induced dichroism of the band upon illumination of the crystal with polarized light having $E \parallel [011]$ and $E \parallel [010]$, together with EPR studies on these anisotropically-bleached crystals, firmly established the connection between these bands and AC oriented along [110] and responsible for the EPR signal of the crystals, i.e., Cl_2^- -centers. Analogous results have also been ob-

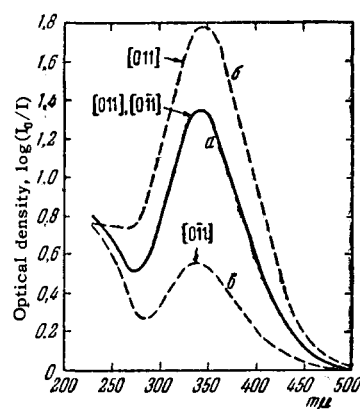


FIG. 13. Absorption spectra of LiF crystals: a) after 30-min x-irradiation at -196°C , measured with polarization along [011] and [0 $\bar{1}$ 1]. After bleaching at -196°C with light polarized along [0 $\bar{1}$ 1]: b) measured with polarization along [011], and c) along [0 $\bar{1}$ 1]. [47]

tained later for other alkali-halide crystals. [47] Figure 13 shows the absorption band of F_2^- in LiF in polarized light before and after illumination with light having $E \parallel [0\bar{1}1]$. While the band for the component with $E \parallel [0\bar{1}1]$ corresponding to the illumination was weakened, an intensity increase was observed in the opposite component. This was due to the fact that the photoexcitation of five groups of the centers oriented along the C_2 axes by light having $E \parallel [0\bar{1}1]$ led to their disruption and reorientation in the [011] direction, upon which the light had no action. The authors note that illumination with polarized light makes it possible to attain a 90% orientation of the AC along a single [110] axis.

The kinetics of reorientation of Hal_2^- molecules was investigated in [47] by studying the degree of induced dichroism as a function of the time elapsed since the anisotropic bleaching and of the temperature. In particular, the "disorientation temperature" T_g was determined, i.e., the temperature at which rapid relaxation of the orientation occurs in centers which have been preferentially oriented in one direction by polarized light at low temperature. This T_g varies for different Hal_2^- molecules over the range from -100°C to -180°C . At temperatures far below T_g (i.e., liquid nitrogen temperature in the cases of F_2^- , Cl_2^- , and Br_2^-), the induced orientation of the centers persisted for indefinite periods. On the basis of studies of the degree of dichroism, these authors [47] determined the absorbing-oscillator type for the Hal_2^- bands. They found both completely anisotropic linear oscillators directed along the axes of the molecules (for the ultraviolet bands) and incompletely anisotropic oscillators (for the visible and infrared bands). Comparison of the observed polarizations of the transitions with the existing theory of spectra of free Hal_2^- molecules permitted them to make a quantum classification of the energy terms of the Hal_2^- molecule-ions incorporated in the structures of alkali-halide crystals.

*In his latest paper, Seitz [44a] considers the V_1 -center to be a halide ion occurring in an interstice surrounded tetrahedrally by regular halide and metal ions.

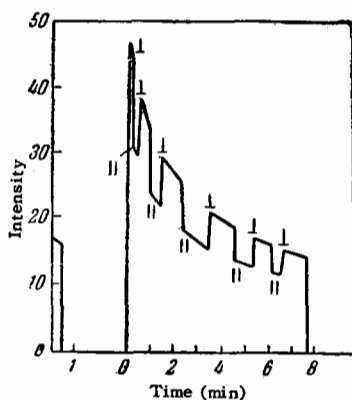


FIG. 14. Polarization of the phosphorescence of x-irradiated crystals bleached by light polarized along [011]. \parallel denotes the intensity with polarization along [011], and \perp along [0 $\bar{1}$ 1].^[46]

Compton and Klick^[34] have studied the symmetry properties of the so-called H-centers by the method of anisotropic bleaching; these centers are formed in the x-irradiation of alkali-halide crystals at liquid-helium temperatures. Induced dichroism in the H-band in KCl and KBr appeared when the vector of the bleaching light was oriented along [100] and [110]. This permitted them to conclude that the absorbing dipole of the H-center is oriented along [110]. This result does not agree with Seitz's^[1] conception of the H-center as a neutral pair of vacancies which has captured a hole (such a system must be oriented along [100] or [111]).

Halperin and Lewis^[48] have studied the anisotropic properties of the centers formed in KCl crystals irradiated with x rays at low temperature after preliminary heat treatment. Anisotropic bleaching of the centers by polarized light was demonstrated by studying the polarization properties of the green phosphorescence of the crystals. Figure 14 shows the phosphorescence curves of a KCl crystal which had been previously illuminated with light having $\mathbf{E} \parallel [011]$, taken in polarized light at various stages in the decay. These authors^[48] ascribe the AC of the green phosphorescence to oxygen incorporated in the structure. However, they give no detailed analysis of the observed polarization phenomena.

A number of studies have been concerned with bleaching in polarized light of the so-called Z-bands in alkali-halide crystals, involving divalent-metal impurities. Remaut and Dekeyser^[49] have observed dichroism in the Z_2 -band in additively-colored NaCl containing SrCl_2 . When the crystal was illuminated with light having $\mathbf{E} \parallel [100]$ in the Z_2 -band, they observed preferential bleaching with the same polarization. Here the amount of dichroism for $\mathbf{E} \parallel [100]$ and $\mathbf{E} \perp [010]$ as a function of the time of illumination went through a maximum. In addition, the induced dichroism vanished upon keeping the crystal in the dark for several hours. These phenomena involve the rapid reorientation of the centers and the

establishment of a uniform distribution of the orientations over the axes of a given order. The existence of dichroism in the Z_2 -band agrees with the anisotropic character of the model of the Z_2 -center proposed by Seitz.

Ishiguro, Sugioka, and Takeuchi^[50] have studied the bleaching in polarized light of the Z_1 - and Z_2 -bands in NaCl and KCl containing strontium. They observed no anisotropic bleaching in the Z_1 -band, in agreement with the EPR experiments on these centers indicating their high symmetry. They observed induced dichroism in the Z_2 -band upon [100]-illumination, both in the Z_2 - and in the F-band. Here in both cases, a dichroism of opposite sign appeared in the F absorption band. There were no anisotropic phenomena upon [110]-illumination. These results provide grounds for concluding that the Z_2 -centers are oriented in the [100] direction. However, the observed characteristics of the bleaching, which showed a complex time- and temperature-dependence, did not permit the authors^[50] to draw final conclusions on the symmetry of the Z_2 -centers. The reason for the correlation of the dichroism in the Z_2 - and F-bands also remains unclear.

Ishiguro and Takeuchi^[51] studied the photo-bleaching of the Z_4 -band in additively-colored KCl containing Sr^{+2} impurity. They discovered and studied the dichroism of the Z_4 -band upon illumination with light having $\mathbf{E} \parallel [100]$ and $\mathbf{E} \parallel [011]$. They observed in both cases a weakening of the absorption for polarization corresponding to the light used for illumination, and a small increase in the absorption for the opposite polarization direction. The authors hence concluded that the Z_4 -centers are directed along [110], in concordance with the previously proposed model of the Z_4 -center as an association of a divalent M^{+2} ion with an adjacent cation vacancy containing a captured electron. In^[51], the appearance of dichroism in the F-band was also observed upon illumination with polarized light in the Z_4 -band, analogously to the phenomenon for the F- and M-bands (see above), which has not yet been explained.

As we see from the studies cited above, research on photochemical transformations in polarized light of complex color centers of various types in ionic crystals has covered a broad scope. A general result of these studies is the demonstration of the anisotropic nature of the transformations of the bands of the centers upon illumination with photochemically-active polarized light. This has also provided a direct experimental confirmation of the hypothesis of the complex anisotropic nature of the color centers, which had been based on indirect data heretofore. In many cases, studies of induced dichroism have resulted in determination of the lattice orientation of the color centers and the oscillator type for the optical transitions. These data have permitted a selection among theoretical models for the complex color centers.

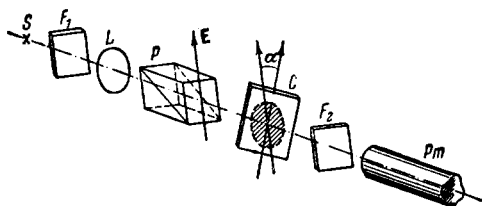


FIG. 15. Diagram of apparatus for observation of the azimuthal dependence of polarization of luminescence.^[52] S – excitation source; F_1 and F_2 – light filters (crossed); L – lens; P – polarizer; C – crystal being studied; Pm – polarimeter.

Studies of the complex kinetics of bleaching in polarized light and of its temperature-dependence have provided information on the nature of the action of light on the color centers, on the mechanism of re-orientation, and other properties of the centers. Finally, the phenomenon discovered in many studies of anisotropic bleaching of the bands of certain centers upon illumination of crystals with polarized photochemically-active light in the region of the bands of other centers has turned out to be very general. This phenomenon, the reasons for which have not yet been finally clarified, indicates interaction of centers of varying types, and provides possibilities for studying this interaction.

3. POLARIZED LUMINESCENCE OF CUBIC CRYSTALS*

The second method of revealing latent optical anisotropy, also based on the anisotropic action of light, is the observation of the polarized luminescence of cubic crystals containing AC. The study of this phenomenon began in 1953, and started the development of the theory of latent optical anisotropy in cubic crystals.

We have seen that with an appropriate relative orientation of the effective vector of the incident light wave and the symmetry axes of the crystal, those AC having a certain orientation in the crystal will absorb light preferentially. Thus, the distribution of the AC which have absorbed light and have thus been excited becomes anisotropic. If the absorbed energy is finally emitted as luminescence, and if in the process of transformation of the excitation energy the spatial anisotropy of the distribution of the centers is not lost, the emitted light may be partially or completely polarized. We can easily verify that when we vary the relative positions of the crystal and of the electric vector of the light exciting the luminescence, the observed degree of polarization of the emission will vary. The corresponding curves, as obtained by observations according to the setup shown in Fig. 15, give the varia-

*A special review published in Usp. Fiz. Nauk in 1956^[52] was devoted to the polarized luminescence of cubic crystals. We therefore limit this presentation to the fundamental assumptions of the method and certain new data (see also ^[19]).

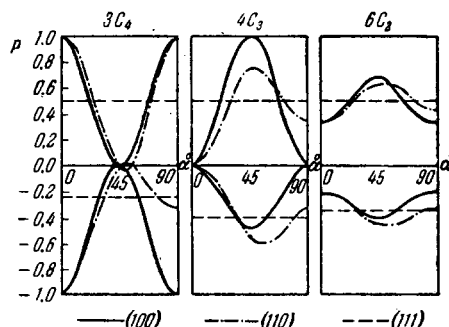


FIG. 16. The azimuthal dependence of the polarization of luminescence when the centers are oriented along the symmetry axes of the different orders. The different lines correspond to different orientations of the crystal plates and different combinations of π - and σ -oscillators.^[54]

tion in the degree of polarization P as a function of the rotation angle α of the crystal plate being studied. This function is commonly called the azimuthal dependence of the polarization of luminescence.

A theoretical calculation of the possible cases of azimuthal dependence may be easily carried out on the basis of the ideas given above (Sec. 1, b) on the anisotropy of the optical properties of individual groups of AC and on the nature of their distribution in the cubic crystals. Such a calculation was carried out in 1953 by Feofilov.^[53,54] It showed that the experimental study of the azimuthal dependence and comparison with the calculated values permits an unequivocal determination of the nature of the distribution of the AC in cubic crystals. Figure 16 shows the azimuthal dependences for completely anisotropic centers oriented along the C_4 , C_3 , and C_2 axes for plates cut from the crystal parallel to the cube (100), rhombic-dodecahedral (110), and octahedral (111) planes. The calculation was performed for the case of linear oscillators for absorption and emission coinciding in direction ($\pi \rightarrow \pi$), and for combinations of linear and circular oscillators (the $\pi \rightarrow \sigma$ and $\sigma \rightarrow \pi$ cases cannot be distinguished).

The method of revealing the latent anisotropy of luminescent cubic crystals by observation of polarized luminescence has been successfully applied in a number of cases to determine the type of orientation of the centers. The greatest number of studies has involved alkali-halide crystals containing color centers or activator centers.

Feofilov^[53,54] has studied the polarized luminescence of color centers in crystals of artificial fluorite (CaF_2) and the alkali fluorides (LiF and NaF). A comparison of the experimental and calculated azimuthal dependences showed that the color centers in these crystals are anisotropic; in CaF_2 they are oriented along the C_4 axes, while in LiF and NaF they are oriented along the C_2 axes. This permitted him to ascribe the observed luminescence to complex color centers, namely the F_2 -centers, i.e., pairs of electrons localized in neighboring vacant anion sites.

Van Doorn^[38] studied the polarized infrared luminescence of M- and R-centers in KCl crystals colored by electrolysis (the maxima of the emission bands were at about 1.06 and 1.24 μ). This study was complicated by the great photochemical sensitivity of the crystals to the light exciting the luminescence. On the basis of a study of the polarized luminescence and induced dichroism, the author arrived at a molecular model for the M-center consisting of a pair of associated F-centers (an F₂-center). The orientation direction for the R-centers turned out to be the C₃ axis, differing from the model for the R-centers proposed by Seitz, which requires orientation along the C₂ axis. In this regard, the author proposed models representing the R-center as a structure containing three electrons (an F₃-center) localized in three neighboring anion vacancies forming a triangle in the (111) plane.

A study of the symmetry properties of F-, M-, and R-color centers in KCl and NaCl by the polarized-luminescence method has also been carried out by Lambe and Compton.^[55] The luminescence of the F-centers (at 1.01 μ for KCl and at 1.2 μ for NaCl) was not polarized, as may be explained naturally by the perfect symmetry of these centers. The M-centers, in agreement with the data of the previous studies, could be represented by the model of dipole oscillators oriented along the C₂ axes. In distinction from the results obtained by van Doorn, these authors found that the R-centers are also oriented along the C₂-axes, in agreement with Seitz's model.

In a later study by Compton and Klick,^[56] also concerned with the R-centers in KCl and NaCl, the discrepancies in the degree of polarization observed in different crystal specimens were so great that the authors concluded that it is impossible in this case to obtain definite information on the nature of the orientation of the R-centers. The observed variations, which explained the discrepancy in the data obtained in ^[38] and ^[55] were ascribed by this author to the interaction of the R-centers with other centers. It was also shown in ^[56] that the N₁-centers in NaCl crystals have symmetry axes oriented along [110].

The anisotropic properties of the M-centers in additively-colored KCl crystals have also been studied by certain Japanese authors.^[39] In agreement with van Doorn's data, a D_{2h} symmetry was ascribed to the M-centers.

The polarized-luminescence method has been applied by Feofilov^[57] to determine the type of orientation of the centers responsible for the line absorption^[58] and emission^[59] spectra of colored LiF crystals. Like the centers giving rise to the broad "red" luminescence band (F₂- or M-centers), these centers were oriented along the C₂ axes.

Besides the centers involving deviations from stoichiometry in the crystal, such as the color centers, the so-called impurity centers due to the presence of

foreign ions in the crystal structure have also been widely studied by the polarized-luminescence method.

Feofilov^[60] has studied the anisotropic characteristics of the trivalent europium ion in the CaF₂ crystal structure. In this case, the azimuthal dependence of the polarized luminescence indicated orientation of the centers along the C₃ axes. From this result, together with the principle of local compensation of excess charge cited in Sec. 1, as well as an analysis of the conditions of preparation of the crystals,^[7] a model for the center possessing the required symmetry could be proposed (see Sec. 1a, Fig. 5).

In an analogous manner, a model for the activator center in single crystals of LiF and NaF activated with hexavalent uranium^[6] was proposed, as has been mentioned in Sec. 1a. In these cases the centers were oriented along the fourfold (C₄) axes. This is consistent with a model in which the excess charge (+5) is compensated by substitution of five O⁻² ions for five of the ions in the first coordination sphere surrounding the U⁺⁶ ion.

A study of the polarized luminescence of color centers in CsI-Tl crystals has shown^[61] that here the luminescent centers are directed along the C₄ axes. In the CsI structure, this corresponds to the cation-cation vector (Fig. 17). This led to the idea of the luminescent color centers in these crystals as being anisotropic structures consisting of Tl⁺ ions isomorphously replacing Cs⁺ ions and associated with other defects localized in the cation sites. In particular, these second defects might also be Tl⁺ ions (see Sec. 1a, Fig. 3).

The luminescent centers excited by short-wavelength light in NaCl-Ag and KCl-Tl, as studied by Tarasova and Feofilov,^[62] turned out to be oriented along the C₄ axes in just the same way. However, in these crystals, the C₄ axis corresponds to the cation-anion vector. The result obtained contradicts the stated assumption that the blue band in the emission spectrum of NaCl-Ag is due to pairs of Ag⁺ ions localized in neighboring cation sites, i.e., oriented along the C₂ axes. The azimuthal dependence of the

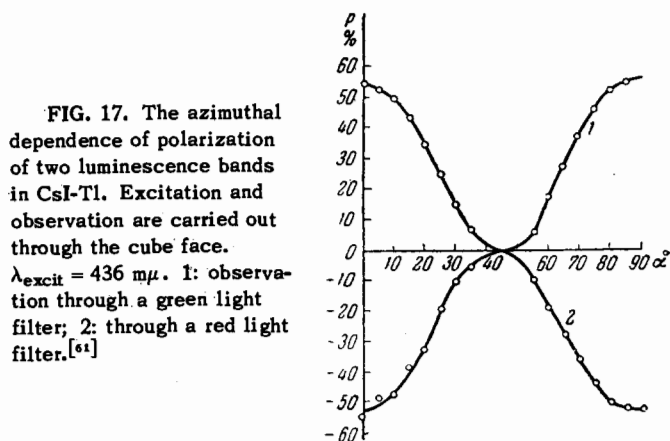


FIG. 17. The azimuthal dependence of polarization of two luminescence bands in CsI-Tl. Excitation and observation are carried out through the cube face. $\lambda_{\text{excit}} = 436 \text{ m}\mu$. 1: observation through a green light filter; 2: through a red light filter.^[61]

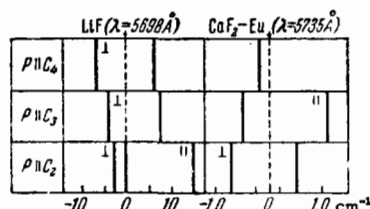


FIG. 18. Diagram of the polarized splitting of the spectral lines of the luminescence of uniaxially-stressed crystals of x-irradiated LiF and CaF₂-Eu.^[73] The dotted lines indicate the positions of the lines in the free crystal.

polarization of the luminescence of KCl-Tl, as demonstrated in this study, showed the inadequacy of the generally-accepted conceptions of the luminescence centers in these crystals as being isotropic entities basically consisting of Tl⁺ ions isomorphously replacing the K⁺ ions.

We can find ways to create a more complete model of the centers in these crystals by analysis of an interesting observation of Klick and Compton made during a study of polarized luminescence.^[63] They found that in certain luminescence bands, a polarization indicating orientation of the centers along the C₄ axes is observed only at liquid-helium temperatures, but vanishes when the temperature is raised to 77°K. This phenomenon was interpreted as indicating a Jahn-Teller-type anisotropy of the emission centers, due to an asymmetric local distortion of the structure near single Tl⁺ ions.

Recently Lushchik and his associates^[64] have performed a detailed study of the polarization characteristics of the luminescence of a number of alkali-halide crystals activated by the "mercury-like" ions Ga⁺, In⁺, Tl⁺, Sn⁺², Pb⁺², and Bi⁺³. At room temperature, the emission from the univalent ions in KCl and KBr crystals was unpolarized. Polarized luminescence was observed with the Bi⁺³ and Sn⁺² centers, and a study showed that these centers were oriented along the C₄ axes. These authors suggested that point defects in the crystal in the vicinity of the Bi⁺³ and Sn⁺² ions hinder the reorientation of the dumbbell-like electron-density of the p-states among the various C₄ axes along which the p-electron cloud of the mercury-like ions is usually extended owing to the Jahn-Teller effect.

West and Compton^[65] have applied the polarized-luminescence method to a study of the anisotropy of Z-centers, i.e., color centers involving the presence of divalent cations in alkali-halide crystal structures. These authors studied the luminescence of Z₂-centers (1.14 μ at 77°K) in KCl-Sr. The lack of any polarization in the emission upon excitation along either [100] or [110] was evidence of the high symmetry of the centers, in the authors' opinion, in better agreement with the model of Pick^[66] than with the model which Seitz^[5] had proposed for these centers.

The existence of polarized luminescence indicating

the anisotropic nature of the centers and orientation along the C₄ axes was demonstrated recently in a study by Alekseeva, Zakis, and Shmit^[67] of crystals activated by Group VI elements (KBr-Se, NaCl-Se, and KI-Te).

A study of the azimuthal dependence of polarization of the luminescence of diamond crystals has been made by Elliott, Matthews, and Mitchell.^[68] They showed that the green luminescence (5032 Å) of crystals which had been subjected to heat-treatment after irradiation with hard radiation was due to anisotropy centers oriented along the C₂ symmetry axes.

The polarized-luminescence method makes it possible to solve another problem related to that of revealing latent anisotropy, namely, determining the elementary-oscillator type of the centers. A simple investigation of the specific features introduced by the orientation of the centers along the crystal symmetry axes permits us to extend the method of polarization diagrams of luminescence proposed by S. I. Vavilov^[69] to the case of luminescence of AC in cubic crystals. Such calculations have been performed by Feofilov,^[70] and have shown that a study of the polarization diagrams makes possible the unequivocal solution of the problem of the elementary-oscillator type in most cases.

This method has been successfully applied to study the elementary-oscillator type of the complex color centers in fluorite crystals,^[71] of Eu⁺³ ions in CaF₂ crystals,^[72] and of U⁺⁶ ions in LiF and NaF crystals.^[6] In the first case, as was expected, it was shown that the luminescence is of electric-dipole type. The same elementary-emitter type was established in the cited reference^[64] for the luminescent centers in KCl-Bi⁺³.

In the luminescence spectrum of Eu⁺³, which is forbidden in the electric-dipole approximation, lines could be found corresponding to all four possible types of dipole emitters: π_e, σ_e, π_m, and σ_m (linear and circular, electric and magnetic). An interesting result was obtained with the crystals LiF-U⁺⁶ and NaF-U⁺⁶. Here each of the spectra exhibited several clearly marked electronic-vibrational series of lines originating from electronic and magnetic linear oscillators, respectively^[6] (see Fig. 19).

The region of applicability of the polarized-luminescence method is naturally limited to the set of luminescent centers. In addition, the luminescence must show an anisotropic spatial distribution, i.e., it must be polarized. While in individual cases the fact itself of whether the emission is polarized or not can be adduced to construct a model for a center (as in the study of West and Compton^[65] on the Z-centers), we cannot in many cases point out unequivocally the reasons for absence of polarization of the emission.

We can point out a number of ways by which the luminescence of AC excited in crystals by polarized light may be depolarized, even when we fulfill all of

the required experimental conditions for observation. First, as was noted in Sec. 1b, the lack of polarization may involve the specific quantum numbers of the combining levels. In particular, the reason for the absence of polarization may be that these levels are degenerate. Besides, as we have seen, a depolarizing effect is exerted by the reorientation of the centers within the lifetime of the excited state, provided that the energy barriers to be overcome in this process are not too high. Obviously, the same result can arise from the migration of excitation energy through the crystal, either owing to an exciton mechanism or to migration of point carriers (electrons or holes). In such a case, the absorption and emission events occur at different centers, and the anisotropy initially created in the distribution of excited centers can be lost in the process of energy transfer.

4. LINE SPLITTING IN THE SPECTRA OF CUBIC CRYSTALS UNDER DIRECTIONAL ELASTIC DEFORMATION (PIEZOSPECTROSCOPIC EFFECT)*

Among the optical phenomena in cubic crystals containing AC expressing the specificity of these centers especially sharply is the "piezospectroscopic" effect in cubic crystals, which has been studied theoretically and experimentally by Kaplyanskii.^[73,74] This consists in the phenomenon of reversible splitting of bands in the spectra of crystals under the influence of directional elastic strains, usually uniaxial compression of the crystal along its symmetry axes. The directional strain here plays the role of the anisotropic influence which must affect differently the groups of centers differing in orientation with respect to the direction of the external influence, which thus serves to resolve these groups (see Sec. 1c).

In principle, uniaxial compression will bring about different shifts in the energy levels of the groups of centers oriented in different ways with respect to the compression axis. Obviously, this must lead to a splitting of a single spectral band of the AC into several components, each of which corresponds to transitions in groups of centers of some definite orientation with respect to the compression axis.

Kaplyanskii^[75,76] has calculated the fundamental characteristics of the splitting of the AC bands under strain for the cases of centers oriented along symmetry axes of different orders (C_4 , C_3 , or C_2), under the assumption that the levels of the individual centers were not degenerate. The splitting was studied for uniaxial compression of the crystal along the four-, three-, and twofold axes.

*Section 4 briefly describes the method and the results obtained thereby. A detailed account of the problem will appear in a special review of studies of the effect of strains on the spectra of crystals, to be published in *Usp. Fiz. Nauk.*

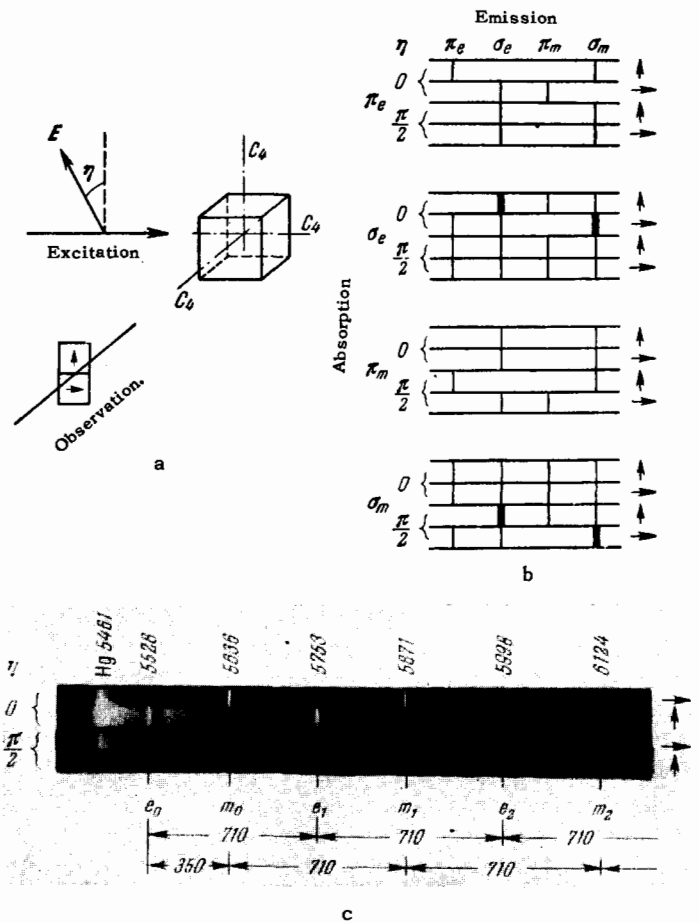


FIG. 19. Determination of the elementary-emitter type of the U^{+6} ion.^[6] a) Diagram of method of observation; b) predicted patterns for various combinations of dipole oscillators; c) spectrogram of the luminescence of a NaF-U crystal taken according to diagram (a) with $Hg_{546m\mu}$ excitation. The electronic-vibrational series of electric (e_0, e_1, \dots) and magnetic (m_0, m_1, \dots) dipoles are clearly visible.

As the calculation showed, the multiplicity (number of components) of the splitting upon deformation along the four-, three-, or twofold axes was completely and unequivocally determined by the lattice orientation of the axes of the centers. The polarization of the split components was completely and unequivocally determined by the multipole type of the corresponding transition ($\pi_e, \sigma_e, \pi_m, \sigma_m$). The magnitude of the splitting as a linear function of the components of the stress or strain tensor in the crystal was determined by two independent parameters when the centers were oriented along the fourfold or threefold symmetry axes, and by three parameters when the centers were oriented along the twofold axes. These "piezospectroscopic" parameters determine the nature of the interaction of the centers with the crystal.

Thus, the study of the effect of directional strains on the spectra of the AC can serve as a method of studying the important characteristics of the centers, such as their lattice orientation, the multipole type of

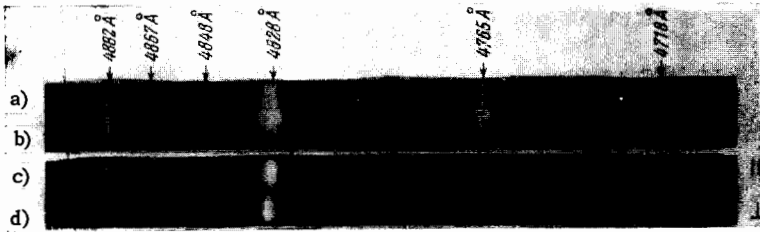


FIG. 20. Spectrograms of the short-wavelength region of the luminescence of LiF-U under uniaxial compression of the crystals along the fourfold symmetry axis ($P \parallel C_4$).^[79] a) Free crystal; b)–d) Crystal under stress; b) in unpolarized light; c)–d) in polarized light.

the transitions, and the interactions of the centers with the crystal.

Recently Kaplyanskii and his associates have studied experimentally the effect of uniaxial compressional strains in crystals on the spectra of local centers for an entire series of crystals: luminescent color centers in LiF,^[77] trivalent rare earths in fluorite,^[78] and hexavalent uranium ions in alkali fluorides.^[79] The studies showed that upon deformation one observes in the spectra of these crystals a reversible splitting of many lines into several polarized components. Here the type of splitting depends essentially on the direction of the compression axis. As a characteristic example of this phenomenon, Fig. 18 shows a diagram of the splitting of the lines of color centers in LiF and of Eu^{+3} in fluorite.^[73] The diagram shows the multiplicity of the observed splitting for strains along the four-, three-, and twofold axes, the polarization of the components in states having the electric vector parallel and perpendicular to the compression axis P (the direction of observation was perpendicular to the compression axis), as well as the amount of splitting for a stress of 10 kg/mm^2 , the splitting depending linearly on the compressive stress.

An analysis of the experimental results showed that they were in complete agreement with the calculated regularities for the anisotropic centers. It was thus shown that the centers for the line spectrum of luminescence of colored LiF are oriented along the C_2 axes, and the optical transitions of the centers are of electric-dipole type. Trivalent rare-earth ions in CaF_2 , in agreement with the results obtained by other methods, are oriented along the three-fold axes, and the transitions may be either electric or magnetic in type. The existence was shown of emission centers of different types in LiF—U,^[79] including ones oriented along the C_4 axes, and the multipole type was determined for a number of lines to be π_e or π_m (Fig. 20). In all of these cases, the nature of the local centers was determined from the data obtained.

We must note a fact which limits the possibilities of the method. First, the splitting effect itself is ordinarily very small. This limits the set of suitable objects for study to crystals having narrow bands in their spectra, and also requires the use of low temperatures and spectroscopic instruments of high dispersion. Second, there are strict demands on the mechanical properties of the crystals, which must maintain rather high elastic strains. However, in

spite of these serious limitations, the study of the effect of directional strains on the spectra may be applied to investigate local centers in a large number of crystals.

An interesting method of studying AC involving application of mechanical effects to a crystal was suggested very recently by Corbett and Watkins.^[80] It consists in the forced orientation of the AC in the crystal along one direction by uniaxial compression of the crystal. In such a uniaxially-stressed crystal, the different axes of the same order are no longer equivalent, and certain orientations become energetically more favorable. Hence, if the centers can reorient easily, a preferred orientation in one direction is created. The degree of preference is determined by a Boltzmann factor containing an energy factor equal to the energy difference between states of differing orientation in the stressed crystal. In particular, the inhomogeneity of distribution can be studied by dichroism of absorption. Such a study with various compression directions may provide information on the degree of lattice orientation of the centers. Corbett and Watkins applied this method to study the centers which arise when oxygen is incorporated into silicon. Here they showed that the centers are anisotropic and oriented along $[111]$. This permitted them to propose a model for the center as being an interstitial oxygen atom bound covalently to two silicon atoms. They were able by the same method to bring about preferred orientation of the superoxide ion O_2^- in the KCl structure.

In his most recent study, Känzig^[83a] has studied by the EPR method the temperature-dependence of the kinetics of such a "mechanical" orientation of the O_2^- radical in potassium halides, and showed that the phenomenon is analogous to paramagnetism ("paraelasticity").

5. LINE SPLITTING IN THE SPECTRA OF CUBIC CRYSTALS IN EXTERNAL MAGNETIC AND ELECTRIC FIELDS

a) The Zeeman effect for anisotropic centers in cubic crystals. Paramagnetic resonance of anisotropic centers in cubic crystals. The latent anisotropy inherent in cubic crystals containing AC can be revealed also by observing the splitting of spectral lines in a magnetic field (the Zeeman effect). As in all of the methods examined above, the possibility of

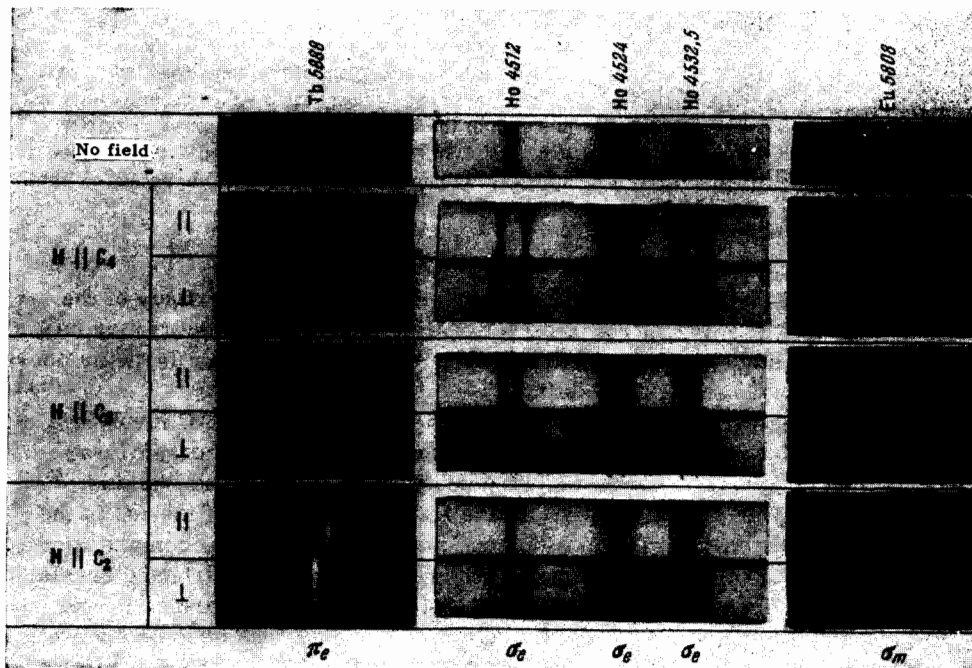


FIG. 21. Splitting of the spectral lines of absorption (Ho) and luminescence (Tb, Eu) for various orientations of CaF₂-RE crystals in a magnetic field. Temperature: -190° C. H = 30 kOe.^[51]

revealing the latent anisotropy here involves the fact that the magnitude of the acting forces is generally different for the groups of centers oriented along the different axes of a given order when anisotropic action is applied to the crystal.

The magnetic splitting of the lines of ions in crystals generally results in a simpler pattern than in the case of free atoms or ions. This involves the partial removal of the degeneracy of the levels due to the intracrystalline electric field. The multiplicity of the remaining degeneracy in anisotropic crystals is not greater than two. In crystals in which a purely cubic field acts on the ions, three- or fourfold degenerate levels may be retained. The cubic crystals containing AC to be studied are equivalent, as we have seen, to macroscopically isotropic superpositions of 12/n anisotropic crystals (three tetragonal, four trigonal, or six orthorhombic) oriented with their axes along the C_n axes of the cubic crystal. Thus, the maximum degeneracy in each group is two. Ions with an even number of electrons (J = integer) can have non-degenerate ($\mu = 0$) and doubly-degenerate ($|\mu| = 1$) states, as was mentioned in Sec. 1b. With an odd number of electrons (J = half-integer), only doubly-degenerate states are possible ($|\mu| = 1/2$ or $3/2$). The crystal quantum number μ characterizing the state of the ion in the crystal obeys the selection rules $|\Delta\mu| \leq 1$. Here the spectral lines which appear in these transitions are polarized along the preferred axis (π -components) if $\Delta\mu = 0$, and perpendicular to it (σ -components) if $\Delta\mu = \pm 1$.

An external magnetic field further lifts the degeneracy. Each of the doubly-degenerate levels is split in the field into two sublevels with $\pm\mu$. The displacements of these sublevels are

$$\delta = \pm g\mu_0 H M_{\text{eff}},$$

and the amount of splitting of the level is $2g\mu_0 H M_{\text{eff}}$, where g is the Landé factor, μ_0 is the Bohr magneton, H is the magnetic field intensity, and M_{eff} is the effective magnetic quantum number of the given level.

If we take into account the selection rules for μ , we can easily check (Fig. 22) that each line (excepting a single case) can split only into a doublet. Only in the case $\mu' = \mu'' = 1/2$ does the splitting give a quartet.

The magnitude of the doublet splitting of spectral lines in a magnetic field is

$$2|\delta' - \delta''| = 2|(g' M'_{\text{eff}} - g'' M''_{\text{eff}}) \mu_0 H,$$

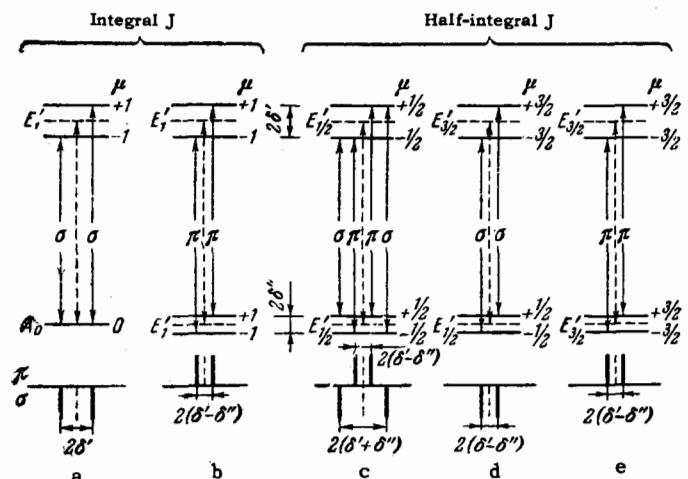


FIG. 22. Diagram of the magnetic splitting of spectral lines in crystals.^[51]

Orientation of the centers along C_3	$H \parallel$	Observation $\perp H$	Polarization \parallel	Electric transitions		Magnetic transitions	
				$\Delta\mu=0 (\pi_e)$	$\Delta\mu=\pm 1 (\sigma_e)$	$\Delta\mu=0 (\pi_m)$	$\Delta\mu=\pm 1 (\sigma_m)$
C_4	\parallel	$\perp H$	\parallel	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$
				$\Delta_0/3$	Δ_0	$\Delta_0/3$	Δ_0
C_3	\parallel	$\perp H$	\parallel	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$
				$\Delta_0/3$	Δ_0	$\Delta_0/3$	Δ_0
C_2	\parallel	$\perp H$	\parallel	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$	$\Delta_0\sqrt{3}$
				$\Delta_0/3$	Δ_0	$\Delta_0/3$	Δ_0

FIG. 23. Calculated magnetic splitting of the spectral lines of centers oriented along the C_3 axes.^[81]

where the primes on g and M_{eff} denote the combining levels. In quartet splitting, the outer components are separated by a spacing $2(g'M'_{eff} + g''M''_{eff})\mu_0H$.

Thus, the pattern of magnetic splitting of spectral lines in crystals is (in a first approximation) considerably simpler than in the case of free atoms and ions.

However, in the cubic crystals under discussion here, the orientation directions of the individual groups of centers (the C_n symmetry axes of the crystal) generally form different angles with the magnetic field H . Hence, the effective value of the magnetic field, as determined by the projection of H on the orientation direction of the centers, will differ for the individual groups of centers of differing orientation. The observed pattern of splitting will be a superposition of several doublets having different spacings between components (including "zero" splitting, if one or several of the orientation axes form angles of $\pi/2$ with H). Hence, we may expect splitting of lines into doublets, triplets, quartets, and quintets (if the "elementary" splitting is of doublet type).

On the basis of these simple ideas on the nature of the magnetic splitting of spectral lines in cubic crystals containing AC, oscillator models of the centers have been used in ^[81] to study the splitting patterns (relative extent of splitting, intensity and polarization of the individual components) to be expected in the various types of orientation of the centers within the crystal (along the C_4 , C_3 , or C_2 axes) for a variety of orientations of the crystal in the external field (with observation direction perpendicular to the field).

As an example, Fig. 23 gives the results of a calculation of the magnetic-splitting pattern for centers oriented along the C_3 axes. This was the most interesting case since comparable experimental data could be obtained. The splitting patterns calculated for different cases of orientation of the centers are sharply qualitatively distinguished from one another. This

permits us to determine the type of orientation of the centers unequivocally from the observed splitting. The observation of magnetic splitting of the spectral lines thereby solves the fundamental problem which arises in the study of latent anisotropy.

We can verify on examining Fig. 23 that the observation of magnetic splitting makes possible the unequivocal solution of another problem, that of determining the elementary-oscillator type. Indeed, the magnetic-splitting patterns of lines corresponding to different changes in the crystal quantum number μ , i.e., to different types of emitters, will differ. The difference in the patterns for electric- and magnetic-dipole transitions does not involve the relative positions of the components, which are determined completely by the displacements of the levels being split. Rather, it involves the polarization of the components as determined by the selection rules, which differ for linear and circular multipoles, and for differing types of transitions (electric or magnetic).

Arkhangel'skaya and Feofilov^[81] have carried out an experimental study of magnetic splitting of spectral lines in artificial crystals of fluorite (CaF_2) containing small amounts of the rare-earth elements. Magnetic splitting could be observed in the absorption spectra of crystals containing neodymium, samarium, holmium, erbium, and terbium, and in the luminescence spectra of crystals containing samarium, europium, terbium, dysprosium, holmium, and erbium. In most cases, individual spectral lines exhibited a distinct pattern (Fig. 21) completely agreeing with that calculated for centers oriented along the C_3 axes. We noted in the previous sections that the same type of orientation of the rare-earth ions in the CaF_2 crystal structure is indicated by observation of the azimuthal dependence of polarized luminescence and by piezo-spectroscopic studies.

In ^[81], data were also obtained on the elementary-oscillator types corresponding to particular spectral lines. In cases in which it was possible to compare them with data obtained by other methods, the results agreed completely.

Unfortunately, this is the only study yet published in which the phenomenon of magnetic splitting of spectral lines was used to study cubic crystals containing AC. In addition, there is some information^[82] on the observation of analogous phenomena in $MgO-Cr$, but there has been no detailed report.

Since the information obtained from the analysis of magnetic-splitting patterns agrees to a considerable extent with that obtained from photochemical studies on polarized luminescence and from the splitting patterns obtained with directional elastic strain, the question naturally arises of comparing these methods. Whereas the limitations of the photochemical and polarized-luminescence methods, which are alluring in their simplicity, involve the presence or absence of the appropriate phenomena, the application of the

methods relying on delicate spectroscopic studies depends on whether the crystals under study possess sufficiently narrow spectral lines sensitive to the appropriate external influence.

The specific factor limiting the possibilities of the magnetic-splitting method must be considered to be the inadequacy of the theory developed in [81]. Thus, at present it does not seem possible to interpret the "anomalous" splitting patterns observed, for example, in the lines in the luminescence spectrum of Sm^{+3} ions in CaF_2 crystals. Also, the complex splitting patterns observed in spectra having a large number of closely-spaced lines are not amenable to calculation. Here the extent of splitting of the levels due to the intracrystalline field is comparable to the splitting in the magnetic field. In this regard, even at relatively low external fields (5–10 kOe), the splitting pattern becomes exceedingly complex. Obviously, a phenomenon is occurring here, analogous to the well-known Paschen-Back effect, which is observed in cases in which the magnetic splitting of the levels of a free atom (or ion) is comparable with the multiplet splitting.

Refinement of the theory should considerably enhance the value of studies using the method of Zeeman splitting of the latent anisotropy of cubic crystals containing AC exhibiting line spectra.

In discussing the Zeeman effect, we must note briefly the existence of another non-optical method of studying the latent anisotropy of cubic crystals involving the application of a magnetic field. Namely, this is the electron paramagnetic resonance of the centers. It is related to the optical methods by the specific effect due to the anisotropy of the centers. This effect is very similar in its characteristics to the optical phenomena in crystals containing AC, in particular the characteristics of the Zeeman effect.

As is known, the appearance of an EPR signal requires that the splitting of a level in a magnetic field owing to the effect of the field on the magnetic moment should be equal to a quantum of energy of the incident high-frequency radiation (the resonance condition) (see, e.g., [83]).

In the anisotropic centers, the g factor of the spectroscopic splitting, which determines the positions of the EPR lines, is anisotropic. Hence, the position of the EPR lines depends on the angle between the axis of the center and the external magnetic field H . Thus, in a cubic crystal containing AC, the EPR spectrum must consist of several lines associated with the individual groups of centers oriented along the several symmetry axes of the same order differing in orientation with respect to the magnetic field. Thus the EPR spectrum must depend strongly on the orientation of the magnetic field in the crystal. Study of this dependence provides information on the lattice orientation of the centers.

A subject of especial interest is the hyperfine structure of the EPR lines of the centers, which involves the

interaction of the electron magnetic moment with the field generated by the nuclear moments. Study of the hyperfine structure permits us to determine with which nuclei the electron in a center interacts, thus giving a direct indication of the Ψ -function distribution and thus of the physical nature of the center itself.

At present there is a large number of studies of the EPR of various impurity and intrinsic defects in cubic crystals, in which data have been obtained on the anisotropic nature of these centers or of the fields acting on them, based on observations of the anisotropy of EPR spectra. Fundamentally, these studies have involved the EPR of ions of the iron group and other groups with incomplete electron shells (see, e.g., the review by Low [84]). An example of a study by the EPR method of AC of a different type is given by the above-mentioned studies of Känzig and his associates. [14, 83a] Here, a detailed study was made of the EPR of hole centers in x-irradiated alkali-halide crystals, and the hyperfine structure was resolved. These latter studies demonstrated the existence of anisotropic hole centers of different types, including anisotropic self-captured holes oriented along the C_2 axes.

EPR is a powerful method of studying the structure of the AC, and also of other centers in crystals. However, obviously, it is suitable only for centers having an uncompensated magnetic moment in the ground state. In addition, its applicability is limited by many factors common to the EPR spectra of crystals, mainly involving various factors broadening the lines.

b) The effect of an electric field on the spectra of anisotropic centers in cubic crystals. We can also use a homogeneous electric field as the external anisotropic influence acting on the AC. In principle, it will cause differing displacements (or splitting) in the levels of the AC belonging to groups oriented differently with respect to the field. This introduces characteristics into the Stark effect in the spectra of the AC of a type such that, generally speaking, a study of this effect will provide information on the centers, in particular, on their symmetry. It is important to note that, in distinction from other methods, which determine only the orientation of the AC, study of the Stark effect permits us to obtain supplementary data on the inversion-symmetry type of the centers. [23]

A well-known theorem in quantum mechanics states that in a system having an inversion center the non-degenerate stationary states have no permanent electric dipole moment. Hence, their spectra must manifest a relatively weak quadratic Stark effect. On the other hand, the states of AC having no inversion symmetry will have a permanent electric dipole moment, and must manifest a relatively stronger linear Stark effect. This permits us to study the Stark effect of the AC in order to resolve the problem of their inversion symmetry.

Overhauser and Rüdhardt [23] investigated the in-

version symmetry of M- and R-color centers in NaCl and KCl by studying the effect of an electric field on the spectra of AC. As was previously shown convincingly in the above-mentioned studies on anisotropic bleaching of M-centers in KCl^[30] and on their polarized luminescence in LiF and NaF^[53,54] and in NaCl and KCl,^[38] the centers responsible for the M-band are anisotropic entities with lattice orientation in the [110] direction. However, if we know only the orientation direction, we cannot choose between several plausible models for the complex centers, all of which have the C_2 axis as their preferred direction (Seitz's models for the M-, R_1 -, and R_2 -centers, as shown in Fig. 2). The centers cannot in principle be distinguished within the framework of polarized-luminescence or polarized-bleaching experiments. As we see from Fig. 2, while the models for the R-centers have inversion centers, the model for the M-center does not have one. Thus, studies of the type of Stark effect in the M-bands may provide information on the inversion symmetry of the corresponding centers, and thus permit us to choose among the hypothetical models.

The symmetry axis of the M-center (in Seitz's model) is a two-fold rotation axis lying in the plane of a triple vacancy. Owing to the symmetry of the center, all its states are non-degenerate; the characteristics of the states have been discussed in a number of theoretical papers.^[22] According to these, the permanent dipole moment of the Seitz M-center is fundamentally directed along the axis of the center in the excited states. The dipole moment of the transition to the first excited state is oriented in the plane of the center in the C_2 direction joining the two negative vacancies.

The Stark displacement in an electric field E of the frequencies corresponding to a transition of an individual center from the ground state to the first excited state is $w = (\Delta\mathbf{p} \cdot \mathbf{E}_{loc})$, where $\mathbf{E}_{loc} = [(\epsilon + 2)/3]\mathbf{E}$, ϵ being the static dielectric constant, and $\Delta\mathbf{p}$ the difference between the dipole moments of the ground state and the excited state. A calculation of $\Delta\mathbf{p}$ using the Ψ -functions of the M-center given in the theoretical study^[22] gives the value $\Delta\mathbf{p} = 5 \times 10^{-18}$ CGS esu. For a field $E \approx 3 \times 10^5$ V/cm, this gives a Stark displacement $w \approx 8 \times 10^{-3}$ eV. Unfortunately, owing to the existence of two possible positions of M-centers along a given [110] axis, the band displacements for these two types of centers are always equal and opposite in direction. Together with the appreciable band width, this leads to a compensation of the linear effect, and gives only a small symmetrical change in the shape of the band involving the centers oriented along the particular C_2 axis. In^[23], the total change in the shape of the absorption band involving all 6×2 groups of centers oriented along the six C_2 axes was calculated; the field direction was taken along [100], and the spectrum was assumed to be observed in a perpendicular

direction, for the case of a Lorentz contour. The results of the calculation showed that an electric field must bring about symmetrical broadening of the bands and the appearance of dichroism. Here the following expression was derived for the relative difference of the absorption coefficients for the polarization states parallel ($\mu_{||}$) and normal (μ_{\perp}) to the external field:

$$\frac{\mu_{\perp} - \mu_{||}}{\mu} = \frac{1}{4} \left(\frac{w}{\Gamma} \right)^2,$$

where Γ is the half-width of the band. For a half-width of the M-band of NaCl at 78°K of 0.05 eV, the relative change $\Delta\mu/\mu \approx 6 \times 10^{-3}$.

A very sensitive method was used to study the phenomenon experimentally, permitting measurement of the dichroism to $\Delta\mu/\mu \approx 3 \times 10^{-5}$. In fields up to 3×10^5 V/cm, no dichroism was noted in the M-band in KCl and NaCl, or in the R_1 - and R_2 -bands in KCl. Thus, any existing dichroism $\Delta\mu/\mu < 3 \times 10^{-5}$, i.e., at least 200 times smaller than the effect which should be observed for the M-centers according to the calculation. Thus, an upper limit was obtained for the permanent dipole moment of the center of 0.4×10^{-18} CGS esu. Likewise, no dichroism was observed when the field direction was along [110]. Thus, the Stark effect in the M- and R-bands provides convincing evidence that the corresponding centers in the alkali-halide crystals possess inversion symmetry. This demands that we reject the Seitz model of the M-center as a triple vacancy which has captured an electron, and give preference to the model of the M-center as a pair of F-centers (an F_2 -center). Such a model is corroborated by the observed lack of participation of M-centers in dielectric losses^[85] and by the lack of magnetic susceptibility^[86] and EPR spectra^[87] of M-centers, and also by the results of studies of the concentration-dependence of the relative intensities of the F- and M-bands.^[88]

This as yet solitary example of an experimental study of the Stark effect in the spectra of AC in cubic crystals demonstrates the potential of this type of study in the investigation of the symmetry properties of the centers. In cases where we can make a theoretical estimate of the effect, even a negative result (in the sense of observing a field effect) permits us to draw important conclusions on the structure of the centers.

* * *

Thus, we have at present an entire arsenal of optical methods for study of local anisotropic centers in cubic crystal structures. With the exception of the paramagnetic-resonance method, perhaps we may state that the optical methods of studying the centers are the only methods in which the anisotropic nature of the centers is manifested in the most direct manner. We have seen that study of various optical phenomena involving the AC, above all, gives us highly

essential information on the symmetry properties and lattice orientation of the centers. Besides, the optical methods permit us to determine the type of the optical transitions, or the multipole type of the corresponding oscillators. The information obtained also includes data on the nature of the interaction of the centers with the crystal structure and its vibrations (from the piezospectroscopic effect) and on the interaction of the AC with light (photochemical transformations). Studies of the optical phenomena permit us to get information also on the properties of reorientation of the centers, as well as on the interactions between centers of differing types.

The revealing of the latent optical anisotropy of cubic crystals containing anisotropic centers thus gives us a variety of information on these centers, permitting us to draw conclusions on the nature and structure of the centers. In addition, we must note the obvious fact that a complete solution of problems involving the nature of local centers in crystals, inevitably requires supplementation of the study of the optical characteristics with the study of other properties. A very important point here is the establishment of a correlation between the physical properties of crystals and the physicochemical conditions under which the local centers were produced in them.

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