Reports of the Academy of Sciences of the USSR

1962

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1962. Vol. 142, No. 2

PHYSICS

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THE PIEZOSPECTROSCOPIC EFFECT IN RUBY CRYSTALS*

(Presented by Academician B. P. Konstantinov, 31 VII 1961)

Numerous works have been devoted to the absorption and emission spectra of Cr^{3+} ions in the corundum lattice α-Al_2O_3 ($^{1-6}$). As has been established, the optical transitions between the levels of isolated Cr ions, split by the intracrystalline field and substituting for Al in the lattice (^{7}), form in the visible spectrum of ruby two groups of narrow lines—the red R-doublet (in emission and absorption) and the B-absorption lines in the blue part of the spectrum—and an intense broad U-absorption band ($\sim 18\,150$ cm^{-1}) with vibrational structure. In the luminescence spectra of specimens with a high Cr concentration, additional numerous long-wavelength lines appear, some of which are also visible in absorption. These lines, among which the so-called N_1- and N_2-lines stand out, are connected, as shown by a study of the concentration dependences of their intensity ($^{4-6}$), with interacting Cr ions.

In the present work, to investigate the nature of the luminescence and absorption centers of ruby, a method was used that had previously been employed to study energy states of various types in cubic crystals (CaF_2—TR, LiF color centers, exciton states of Cu_2O, LiF—U, etc.) ($^{8-10}$). The method consists in studying the influence of directed elastic deformations on the spectra of crystals. Directed deformation, by lowering the symmetry of the crystal, removes the existing degeneracy of energy states and thereby leads to splittings, as well as to shifts in the spectra (“piezospectroscopic effect”); the study of this effect provides valuable information about the most diverse energy states of crystals.

The experimental procedure was analogous to that described in (^{8},^{9}). Oriented** single crystals of synthetic ruby (Cr concentration 1.6%) in the form of elongated rectangular parallelepipeds were subjected in a special press at a temperature of 77° K to uniaxial compression along the long side. The specimens were oriented in such a way that the vertical compression axis P was either parallel to the optical axis of the crystal ($P \parallel C_3$), or lay in the basal plane of the crystal perpendicular to C_3 ($P \perp C_3$). In the latter case the axis

Fig. 2. Lattice of α-Al_2O_3 and directions of the compression axis (in the plane C_3). Different sizes of the black circles denote two Al layers, slightly displaced along C_3; white circles—O.

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P was directed both along one of the three second-order symmetry axes lying in the basal plane ([11]) ($P \parallel C_2$) and perpendicular to them ($P \perp C_2$). The direction of observation L was transverse with respect to P ($L \perp P$); in the case $P \parallel C_3$ it was arbitrary, while for $P \perp C_3$ observations were made in two mutually perpendicular directions: $L \parallel C_3$ and $L \perp C_3$. The spectra of the uniaxially stressed crystals were photographed in polarization states with $E \parallel P$ and $E \perp P$ on a spectrograph with a dispersion of ~ 2.5 Å/mm.

As a result of the investigation it was established that uniaxial-compression deformation exerts a substantial reversible influence on all, without exception, elements of the structure of the absorption and luminescence spectra of ruby. The character of the influence is different for different lines and depends sharply on the direction of the axis P. For $P \parallel C_3$ (the symmetry is not changed) only shifts of lines in the spectra are observed, whereas for $P \perp C_3$ (lowering of symmetry) both shifts and splittings of lines occur.

R- and B-lines. Uniaxial-compression deformation causes only a shift of the lines R_1, R_2, B_1, B_2. This shift, for all three directions of compression, occurs for the R-lines toward the long-wavelength side and differs somewhat in magnitude for R_1 and R_2. For the B-lines the shift, identical for B_1 and B_2, occurs toward the short-wavelength side for $P \perp C_3$, and toward the long-wavelength side for $P \parallel C_3$. The shift of the R- and B-lines varies linearly with the stress of uniaxial compression p; moreover, the magnitude of the shift for $P \perp C_3$ does not depend on the direction of the compression axis in the basal plane.

Fig. 2. Lattice of α-Al_2O_3 and directions of the compression axis (in the plane $\perp C_3$). Different sizes of the black circles denote two Al layers, slightly displaced along C_3; white circles—O.

The observed absence of splitting of the R- and B-lines under deformation of the crystal is in agreement with the interpretation of these lines ([7]). According

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* The results of the work were reported at the 10th All-Union Conference on Luminescence, Moscow, June 1961.

** Determination of the direction of the C_3 axis in single crystals was carried out optically, by birefringence and dichroism, and determination of directions in the basal plane from asterism figures upon reflection of light from the etched surface ([11]).

Figure 1. Splitting of the N_1 luminescence line in uniaxially stressed ruby crystals

Figure 2: Figure 1. Splitting of the N_1 luminescence line in uniaxially stressed ruby crystals

to (^{7}), the levels of single Cr^{3+} ions participating in the formation of the R- and B-lines possess only Kramers degeneracy. Therefore deformation of the crystal, which reduces to the action of an intracrystalline electric field, can lead only to a shift of the levels, and consequently of the lines. From symmetry considerations it follows that for this case the shift of the lines $\Delta\nu = \nu(p) - \nu(0)$, as a linear function of the stresses, is expressed by a relation of the form

$$\Delta\nu = A(\sigma_1 + \sigma_2) + B\sigma_3.$$

Here $\sigma_1, \sigma_2, \sigma_3$ are the normal stresses in the Cartesian coordinate system X_1, X_2, X_3, oriented in the crystal analogously to (^{12}) (X_3 along C_3; X_1 along C_2, $X_2 \perp C_2$ in the basal plane), and A and B are certain parameters. The experimental results, in particular the independence of the shift from the direction of P for $P \perp C_3$, agree with this relation. The found values of the shift parameters (in $\mathrm{cm}^{-1}/(\mathrm{kg/mm}^2)$) for the R_1-line are:

$$A = -0.031, \qquad B = -0.014;$$

for the R_2-line:

$$A = -0.027, \qquad B = -0.019.$$

The expected shift of the lines $d\lambda^{-1}/dp$ for hydrostatic compression ($\sigma_1 = \sigma_2 = \sigma_3$), determined from this and equal to $2A + B$, proved to be $7.6 \cdot 10^{-4}$ cm^{-1}/at for R_1 and $7.3 \cdot 10^{-4}$ cm^{-1}/at for R_2, in good agreement with experiments (^{13}) ($-7.5 \cdot 10^{-4}$ and $-6.7 \cdot 10^{-4}$, respectively).

N_1-line. For $P \perp C_3$ ($P \parallel C_2$) or $P \perp C_2$, a doublet splitting of the line is observed (Fig. 1). For $P \parallel C_2$ the center of the doublet is shifted somewhat toward the long-wavelength side, and the doublet is polarized in such a way that in $E \parallel P$-polarization, for $L \parallel C_3$ and $L \perp C_3$, both components are invariably observed, the short-wavelength one being the more intense. In $E \perp P$-polarization only the long-wavelength component appears, which is intense for $L \parallel C_3$ and disappears when the direction L is changed by 90° ($L \perp C_3$). For $P \perp C_2$ a sharp shift of the center of the doublet toward the long-wavelength side is observed, and its polarization is such that in $E \parallel P$-polarization, for $L \parallel C_3$ and $L \perp C_3$, one short-wavelength component of the doublet is observed. In $E \perp P$-polarization for $L \parallel C_3$ a doublet is observed with a more intense long-wavelength component, which disappears on going to $L \perp C_3$. For $P \parallel C_3$ there is only a long-wavelength shift of the N_1 line. The magnitudes of the shifts of all components of the splitting from the position of the line in the free crystal $\Delta\nu$ depend linearly on p.

Figure 3. Luminescence spectrum of ruby in uniaxially stressed crystals,
$P \parallel C_2,\ L \parallel C_3$

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Fig. 1. Splitting of the N_1 luminescence line in uniaxially stressed ruby crystals

Fig. 3. Luminescence spectrum of ruby in uniaxially stressed crystals, $P \parallel C_2,\ L \parallel C_3$

As already indicated, studies of the N_1 line (^{5,6}) convincingly show that it belongs to complex formations arising from the interaction of Cr ions. We shall show that the described pattern of splitting of the N_1 line under deformation can be entirely explained on the assumption that N_1 is associated with pairs of Cr ions that replace two Al ions nearest to one another, lying in the α-Al_2O_3 lattice in one plane normal to C_3.

Figure 2 shows a scheme of the arrangement in the lattice of Cr ions, which are located in the octahedral voids of the closest hexagonal packing of oxygen ions. It schematically indicates the nearest pairs of Al ions located in one plane ($\perp C_3$) (connected by a solid line), from which it is seen that the pairs of Cr ions replacing them form three equivalent groups of chromium "molecules" (marked in the figure with Roman numerals), differing in orientation in the basal plane. The situation here is analogous to the case of the so-called anisotropic centers in cubic crystals ("orientational" degeneracy), studied in detail in (^{8,9}), which made it possible to apply, similarly to (^{8,9}), a treatment of the problem of the effect of deformation on the spectrum of linear centers of Cr^{3+} pairs.

The splitting of the N_1 line observed for $P \perp C_3$ can naturally be explained by the different action of the deformation on Cr^{3+} pairs oriented differently with respect to P, as a result of which the transition frequency in the N_1 line becomes different for different groups of "molecules." It is easy to see (Fig. 2) that for $P \parallel C_2$ and $P \perp C_2$ a doublet splitting of the line should occur, since in both cases the pair centers, with respect to P, make up two classes of centers whose axes form the following angles with P: for $P \parallel C_2$, 0° (group I) and 60° (II–III); for $P \perp C_2$, 90° (I) and 30° (II–III). We carried out a control experiment in which the compression axis P (shown by a dashed line in Fig. 2) made different angles (I –45°, II –75°, III –15°) with all three groups of centers; in accordance with this, a triplet splitting of N_1 was observed (Fig. 1). For $P \parallel C_3$, evidently, no splitting should occur, since all three groups of centers are in the same position. Each component of the splitting can, on the basis of its intensity, as well as its polarization and shift (see below), be assigned to the corresponding group (or groups) of pair centers. The numbers of these groups, for their arrangement and P according to Fig. 2, are indicated in Fig. 1 for each splitting component.

Taking into account the polarization of the N_1 line in a free crystal ($E \perp C_3$), it is natural to assume that the optical transition in an individual Cr^{3+} pair corresponds to a linear electric dipole oscillator directed along its axis. In this case it is easy to calculate the spatial distribution of the radiation of the individual groups of pair ions and, consequently, to find the polarization of the splitting components associated with these groups. In Fig. 1, at the top near each splitting component for $P \parallel C_2$ and $P \perp C_2$ associated with certain (I or II–III) groups, the numbers in parentheses indicate its calculated relative intensity for the given polarization states and observation direction. Comparison of the experimental and calculated values of the polarization of the splitting components reveals their good agreement.

Finally, from symmetry considerations it follows that for $P \perp C_3$ and $P \parallel C_3$ the shift $\Delta\nu$ of the transition frequency in a linear center lying in the basal plane can be expressed as $\Delta\nu = A_{\parallel}\sigma_1 + A_{\perp}\sigma_2 + B\sigma_3$, where σ_i are the normal stresses in the coordinate system of the center (X_1 is the axis of the center; X_2 is the direction perpendicular to it in the basal plane; X_3 coincides with C_3). Starting from this relation, one can, for $P \perp C_3$, calculate $\Delta\nu$ for individual groups of centers for $P \parallel C_2$ and $P \perp C_2$ ($\sigma_3 = 0,\ \sigma_1 = p\cos^2(\widehat{PX_1}),\ \sigma_2 = p\cos^2(\widehat{PX_2})$), expressing them through the parameters $A_{\parallel}$ and $A_{\perp}$. Table 1 gives a comparison of 7 experimental values of the shifts of the components (for $p = 100$ kg/mm^2) with the calculated $\Delta\nu$ for the corresponding

and by groups of centers. This comparison, for the values of the two parameters (in $\mathrm{cm}^{-1}/\frac{\mathrm{kg}}{\mathrm{mm}^2})A_{\parallel} = 0.053;\ A_{\perp} = -0.117$, reveals mutual agreement. The value determined from the shift for $P \parallel C_3$ is $B = -0.074$.

Thus, the multiplicity of the splitting, the magnitudes of the shift, and the polarization of the splitting components of the N_1 line under deformation agree well with the calculated picture of the phenomenon for centers that are complex in structure and form several equivalent groups differing in direction in the basal plane.

Table 1

	$P \parallel C_2$	$P \parallel C_2$	$P \perp C_2$	$P \perp C_2$	$\angle PC_2 = \pi/4$	$\angle PC_2 = \pi/4$	$\angle PC_2 = \pi/4$
	I	II–III	II–III	I	III	I	II
Exp.	4.6	−7.1	1.0	−12.5	4.6	−2.8	−10.6
Calc.	5.3	−7.4	1.1	−11.7	4.1	−3.2	−10.4

This serves as convincing evidence of the connection of N_1 with such centers, which are most likely the pairs of Cr^{3+} considered above.*

Other lines. Splitting under deformation $P \perp C_3$ is observed for a large number of weaker narrow luminescence lines located between R_1 and R_2 and in the longer-wavelength part of the spectrum (see Fig. 3).** The splitting pattern of these lines is sharply individual; it is complex and different for $P \parallel C_2$ and

$P \perp C_2$, and both doublet and triplet (for example, for N_2) splitting of the lines is observed; the splitting components are polarized. It should be noted that the magnitude of the splitting of these lines is, as a rule, considerably smaller than for N_1, which in many cases did not make it possible to obtain satisfactory resolution of the split components. Therefore, further studies are required in order to obtain the complete picture and its interpretation. Apparently, the weak lines are associated with complex centers differing in structure and arising through the interaction of Cr ions, which accounts for the complexity and variety of the splitting pattern under deformation. From comparison of the pattern in polarized light for $L \parallel C_3$ and $L \perp C_3$, it can already be concluded that all ruby lines that split under deformation have an electric-dipole nature.

The authors express their gratitude to E. F. Gross for his interest in the present work and to Yu. E. Svetlov for discussion of its results.

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Received
31 VII 1961

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* It should be noted that there is some ambiguity in the choice of the specific model of the pair center. In particular, the phenomenon can formally be explained by assuming that N_1 is associated with nearest-neighbor Al pairs substituted by Cr (in Fig. 2 connected by a dotted line), if one neglects the small inclination of these pairs to the basal plane and assumes that the oscillator of the transition in the center is perpendicular to the axis of the pair and to C_3.

** Doublet splitting under $P \perp C_3$ was also observed for the head member of the electron-vibrational structure of the intense green U-band.

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