

Optical Properties and Crystal Chemistry of Synthetic Rutile Implanted with Cobalt Ions

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Abstract—Implantation of high-energy cobalt ions into plates of synthetic rutile has been studied, and absorption, luminescence, and luminescence excitation spectra have been recorded and interpreted. Long-wave luminescence (820 nm) of $\text{Ti}_{\text{IV}}^{3+}$ ions in rutile has been revealed; its intensity increased after the cobalt implantation. Analysis of luminescence and luminescence excitation spectra has allowed us to specify the scheme of electron energy levels of rutile and to establish the energy levels of impurity Ti^{3+} ions occupying vacant octahedrons with the C_{2h} symmetry in structure of the mineral.

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INTRODUCTION

Rutile is widespread in nature. It occurs in igneous and metamorphic rocks, pegmatites, and hydrothermal and other rocks. In many cases, this mineral is an indicator of typomorphic features of mineral formation. Spectroscopic properties of rutile reflecting crystallochemical features of its structure can enhance its typomorphic importance. However, they are still poorly studied (Marfunin, 1974; Platonov, 1976; Tarashchan, 1978; Gaft et al., 1980, 1981; Gorobets and Rogozhin, 2001). Therefore, we carried out a comprehensive optical spectroscopic study of synthetic rutile. In gemology, synthetic rutile originally obtained in 1948 is known to be the first among numerous diamond imitations.

The space group of rutile is $P4_2/mnm$. The TiO_6 octahedrons linked by opposite edges in columns parallel to axis C of crystal are the basis of mineral structure (Minerals, 1965). Columns are linked by octahedron tops. All TiO_6 octahedrons are structurally equivalent, have the D_{2h} symmetry, and are elongated along their principal axis Z , which is oriented parallel to $[1\bar{1}0]$ and $[110]$. The electron structure of rutile was described in detail by Tossel and Vanghan (1974), who developed a scheme of energy levels of the rutile molecular orbitals (Fig. 1) adopted in this study. The scheme was based on theoretical calculations and experimental data, including photoelectron, optical, and X-ray spectroscopy. This scheme comprises the upper part of the valence band and the lower part of the conduction band of this mineral.

SETTING OF PROBLEM AND EXPERIMENTAL

The objective of this study was to conduct high-energy implantation of cobalt ions into plates of synthetic rutile and investigate these plates using comprehensive optical spectroscopic techniques. The final goal was to study the effect of the cobalt ion implantation on optical properties of synthetic rutile.

The technique of high-energy ion implantation that has widely been used in different natural sciences since the early 1960s allows the implantation of a dosed amount of a certain chemical element into the near-surface layer of any solid matrix with a high precision. Postimplantation heat treatment of irradiated crystal is presumed for distribution of the implanted chemical element in the material volume. The survey of publications indicates that ion implantation into a mineral matrix is not carried out systematically. Ohkubo et al. (1986), Saito et al. (1991), Lopatin et al. (2001, 2002, 2005), and Khaibullin et al. (2003) demonstrated the fundamental possibility to modify physical properties of minerals and their synthetic analogues, particularly coloration, with implantation of ions of the iron group elements.

Crystal plates of colorless synthetic rutile cut out parallel to $\{100\}$ and $\{001\}$ were irradiated with the flux of Co^+ ions, which was forced by an electric field with voltage 40 kV on an ILU-3 ion-beam accelerator. The radiation dose was 1.5×10^{17} ion/cm². Postimplantation annealing was carried out in air at 950°C for one hour. The initial, implanted, and annealed rutile samples were studied with absorption spectroscopy on a Hitachi-330 spectrophotometer and a special optical spectroscopic device used the technique previously described by Bakhtin et al. (1997). In addition, luminescence and luminescence excitation spectra of all

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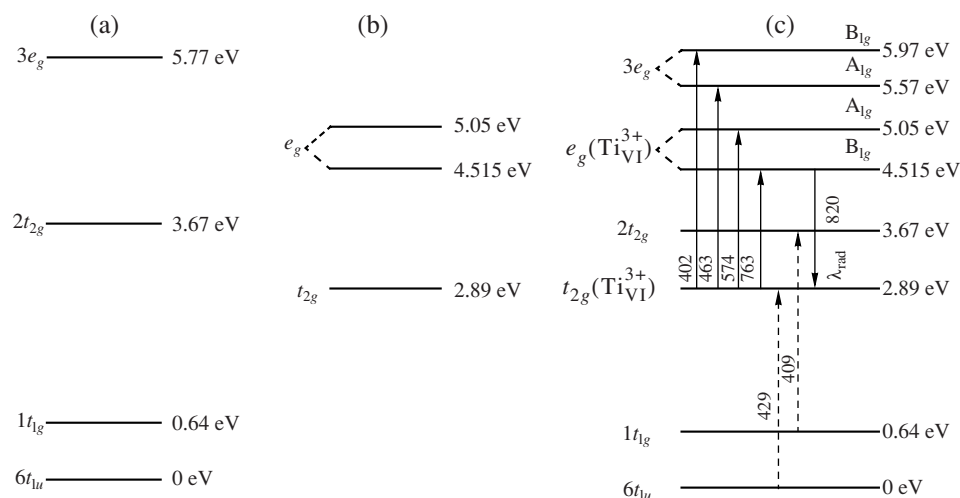


Fig. 1. Energy levels (eV) in rutile: (a) levels of molecular orbitals; (b) levels of $\text{Ti}_{\text{IV}}^{3+}$ impurity ions; (c) general scheme of the $\text{Ti}_{\text{IV}}^{3+}$ - bearing rutile levels. Solid arrows show electron transitions and corresponding wavelengths exciting luminescence of rutile; dashed arrows indicate transitions developing in absorption spectra of rutile.

samples were recorded with a KSVU optical spectroscopic system. Photoluminescence spectra were recorded within the range 250–1000 nm at 77 K. X-ray analysis with a DRON-3M diffractometer was carried out to detect newly formed mineral phases that could be formed in rutile as a result of implantation and annealing.

RESULTS AND DISCUSSION

After the high-energy implantation of Co ions, the initially colorless plates of synthetic rutile have darkened and acquired grayish hue with metallic luster. Such modifications of colorless transparent dielectrics resulting from radiation damage of near-surface zones of irradiated particles and formation of nanoscale zones of implanted impurity are well known and described in the literature. Samples of {100} rutile plates have acquired a green tint after postimplantation annealing, whereas {001} plates of the same crystals have become reddish orange.

The typical optical absorption spectrum of initial colorless plates of rutile (Fig. 2a) is characterized by strong ultraviolet absorption as self-absorption of the mineral caused by transition of an electron from the valence band to conductance band. The long-wave edge of this absorption occurs at 410 nm and corresponds to an electron transition from the $1t_{1g}$ level formed by 2p-orbitals of oxygen at the limit of the valence band to the $2t_{2g}$ level at the bottom of the conductance band in the electron scheme of molecular orbitals (Fig. 1). The energy of this transition is 3.03 eV, and the absorption edge at 410 nm observed in optical spectra corresponds to this energy. The absorption decreases sharply within the visible region of the rutile spectrum, and no selective absorption bands are noted. In optical spectra of the Co-implanted rutile samples, which are gray and with

metallic luster, the absorption in the visible region abruptly increased, but selective absorption did not appear (Fig. 2, curve b).

As was mentioned above, after the heat treatment, the color of rutile plates was changed to greenish or orange depending on the crystallographic orientation of the plates in the mineral crystals. Their optical spectra were also significantly modified (Fig. 2, curves c and d). In particular, the region of short-wave absorption of the mineral was expanded significantly and its long-wave edge was extended into the green region of the spectrum (500 nm) in {100} plates and to the orange region (580 nm) in {001} plates. A broad bend at 430 nm (2.88 eV) is noted at the declination of the curve of this absorption. This bend is a maximum for an additional

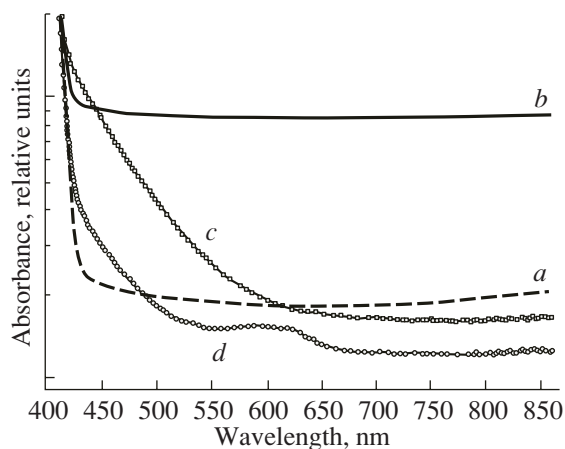


Fig. 2. Absorption spectra of rutile: (a) before implantation; (b) after implantation with cobalt ions; (c) after implantation and annealing, orange {001} plate; and (d) after implantation and annealing, greenish {001} plate.

broad absorption band that has been superimposed on the edge of the mineral self-absorption and extending to the green and orange regions of the spectrum, causing the color of {100} and {001} plates of rutile, respectively. This absorption band can be attributed to an electron transition of the ligand $\rightarrow$ metal type and related to an electron transition from the $6t_{1u}$ level of 2p-orbitals of the oxygen valence band to the t_{2g} level of 3d-orbitals of Ti_{IV}^{3+} ions, which can arise in a significant amount in the process of rutile implantation due to the capture of electrons driven out from oxygen by titanium. The energy position of this absorption band is explained by the distribution of the Ti_{IV}^{3+} energy levels in the rutile electron structure [in the system of molecular orbitals (MO) TiO_2] that is discussed below.

In addition to the broad bend at 430 nm at the declination of short-wave absorption, the narrow absorption bands at 445, 465, and 475 nm and the broad absorption bands at 500, 620, 660, 1400–1450, and 2150 nm as sinuous flexions are observed in optical spectra of implanted and annealed rutile. Since the samples have been implanted with Co ions, it is reasonable to assume that the additional absorption bands are related to cobalt ions. Bivalent cobalt with the $3d^7$ electron configuration is the most stable and induces three broad spin-permitted absorption bands. The location of these bands is defined by specific crystal field parameters. For octahedral coordination, these absorption bands occur normally at 500, 700, and 1400 nm, and for tetrahedral coordination, at 660, 1400–1500, and 2300–2500 nm (Pappalardo et al., 1961; Zimring and Stont, 1969; Marfunin, 1974; Platonov, 1976; Sviridov et al., 1976). This indicates that the position of broad absorption bands in optical spectra of the cobalt-implanted rutile is close to the location of cobalt absorption bands in other compounds and minerals, which, in turn, allows these bands to be interpreted as absorption bands of bivalent cobalt ions. Furthermore, five or six broad absorption bands of bivalent cobalt ions in the rutile spectrum and the wide waveband of their position support the occurrence of Co^{2+} ions in both octahedral and tetrahedral coordinations of the oxygen anions. It is interesting that an impurity of bivalent cobalt ions in tetrahedral sites results in appearance of broad spin-permitted bands at 615, 1480, and 2520 nm in the optical absorption spectrum of the $ZnAl_2O_4$ spinel (Ferguson et al., 1969). Thereby, the absorption band at 2520 nm is accompanied by vibrating replication at 2146 nm. Assuming that band at 2150 nm in the optical absorption spectra of rutile samples is a vibrational repetition of electron transition, the latter should generate an absorption band at 2520 nm. The increase in absorption from 2100 nm to the long-wave limit (2500 nm) of waveband indicates indirectly the presence of such a band. Taking these remarks into account, it may be deemed that the broad absorption bands at 620, 1400–1450, 2150, and 2520 nm in optical spectra of the Co-

implanted rutile practically coincide with similar absorption bands of Co_{IV}^{2+} in the spinel spectrum. This allows us to suggest that the Co-bearing spinel phase Co_2TiO_4 formed owing to implantation occurs in the studied rutile. This newly formed spinel phase contains bivalent cobalt ions in both octahedral and tetrahedral structural sites.

The presence of the spinel phase has been verified with XRD. The X-ray diffraction pattern of {100} plate of implanted and thermally treated rutile shows an additional peak at 0.254 nm, which can be attributed to reflection 311 of spinel phase Co_2TiO_4 formed in rutile during annealing and crystallization of a domain that became amorphous during implantation.

The aforesaid indicates that absorption bands at 620, 1400–1450, and 2520 nm in optical spectra of the Co-implanted synthetic rutile can be related to electron transitions in the cobalt ions occupying tetrahedral sites in the structure of the spinel that occurs as inclusions in rutile. In character and position in spectra of the Co-implanted rutile, the broad absorption bands at 500, 660, and 1400–1450 nm correspond to absorption bands of Co_{VI}^{2+} ions occupying octahedral sites in the spinel structure. The electron transitions that correspond to the broad absorption bands of the bivalent cobalt ions in optical spectra of rutile and calculated crystal-field parameters Dq and B in the Co_{VI}^{2+} and Co_{IV}^{2+} ion sites are listed in Table 1; they confirm the interpretation presented above. The narrow bands at 445, 465, and 475 nm in optical spectra of implanted rutile can be related to spin-forbidden electron transitions in the Co_{VI}^{2+} and Co_{IV}^{2+} ions (spinel inclusions) from the main state to levels of terms ^2P , ^2H , and ^2G .

The studied rutile samples are distinguished by photoluminescence with emission in the near-IR region of spectrum with a maximum at 830 nm (Fig. 3). Both initial and implanted rutile specimens displayed luminescence. The intensity of luminescence of the implanted samples is 3–5 times higher than that of the initial samples. The excitation band 820 nm (12195 cm^{-1}) is slightly asymmetric and is characterized by broader long-wave side. A wavelike bend at 850 nm (11765 cm^{-1}) is marked approximately at half-height of the peak. This bend indicates that the excitation band consist of two components differing in energy of 430 cm^{-1} . Three vibrating frequencies 427, 571, and 730 cm^{-1} are detected in the IR spectrum of rutile (Minerals, 1965). One frequency practically coincides with splitting of the rutile luminescence band. This indicates that, in addition to the electron transition responsible for the radiation band 820 nm, a vibrating repeat is displayed in the spectrum at 850 nm.

The total half-width of the rutile luminescence band is about 800 cm^{-1} . The rather complex excitation spectrum of rutile is shown in Fig. 4. The lowest energy

Table 1. Positions of broad electron absorption bands in spectra of Co-implanted rutile and their interpretation fitted in cubic symmetry field

Position of bands		Nature of bands	Electron transition	Calculated values (cm ⁻¹) of frequencies of transitions and Dq and B parameters of crystal field	
nm	cm ⁻¹			Co _{VI} ²⁺	Co _{IV} ²⁺
500	20000	Co _{VI} ²⁺	${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	20040	
620	16130	Co _{IV} ²⁺	${}^4A_2(F) \longrightarrow {}^4T_1(P)$		16040
660	15150	Co _{VI} ²⁺	${}^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$	15120	
1400–1450	7140–6900	Co _{VI} ²⁺	${}^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$	7020	
		Co _{IV} ²⁺	${}^4A_2(F) \longrightarrow {}^4T_1(F)$		6910
2520	3970	Co _{IV} ²⁺	${}^4A_2(F) \longrightarrow {}^4T_2(F)$		4000
				$Dq = 810$ $B = 940$	$Dq = 400$ $B = 730$

exciting luminescence of rutile corresponds to the band 763 nm (13105 cm⁻¹); hence, the Stokes shift is 910 cm⁻¹. The low value of the Stokes shift and the moderate half-width of the luminescence indicate that radiation is of intracenter nature and pertains to a d-element of the transitional group. Taking into account that both Co-implanted samples and initial plates of pure rutile are luminescent, luminescence at 820 nm should be attributed to titanium. Since the Ti⁴⁺ ion distinguished by empty d-orbitals cannot induce intracenter luminescence, the latter should be attributed to Ti³⁺ ions, which commonly occur as an impurity in both natural and synthetic rutile (Sviridov et al., 1976). In the crystal field of cubic symmetry, Ti³⁺ d-orbitals split onto two clusters t_{2g} and e_g occurring apart from each other at the $10Dq$ value equal to about 20000 and 9000 cm⁻¹ for an

octahedron and tetrahedron, respectively. Therefore, a Ti³⁺ ion in a tetrahedral site cannot induce the luminescence 820 nm. This luminescence should be attributed to trivalent titanium in octahedral sites of the rutile structure. The upper level e_g of d-orbitals in an octahedron is split by low-symmetrical crystal-field components into two levels. During compression of the octahedron, the upper level will correspond to the d_{z^2} orbital (symmetry a_{1g}), and the lower level, to the $d_{x^2-y^2}$ orbital (symmetry b_{1g}). These sublevels change places in an elongate octahedron. The lower t_{2g} set of Ti³⁺ d-orbitals at slight distortion of the octahedron is

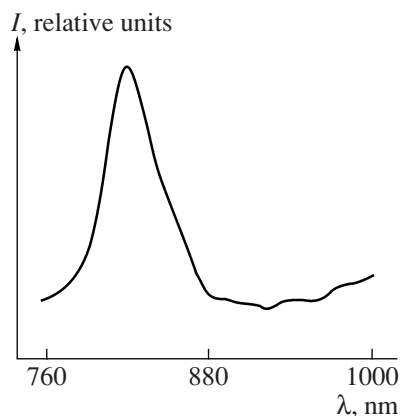
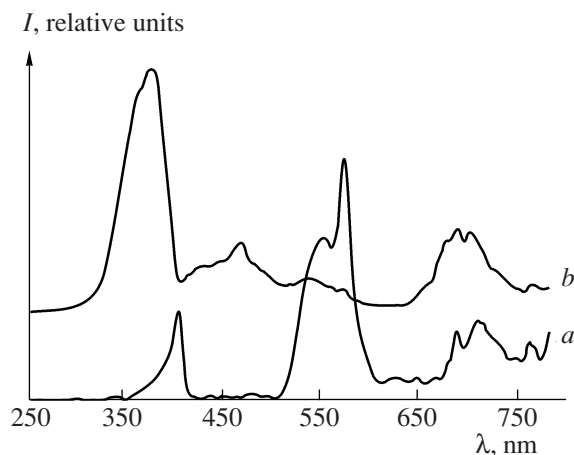
**Fig. 3.** Luminescence spectrum of rutile.**Fig. 4.** Luminescence excitation spectra of rutile: (a) after implantation of cobalt ions into rutile and (b) after implantation of cobalt ions into rutile and annealing.

Table 2. Positions of absorption bands in luminescence excitation spectra of rutile ($\lambda_{\text{rad}} = 820$ nm)

Position of bands		Electron transition $t_{2g}(\text{Ti}_{\text{VI}}^{3+}) \rightarrow$	Frequencies (cm^{-1}) that cause vibra- tional repetitions of electron transition
nm	cm^{-1}		
380	26315	$b_{1g}(3e_g \text{ MO TiO}_2)$	$571 + 2 \times 427$
387	25840		$427 + 571$
402	24875		
423	23640		$571 + 2 \times 730$
437	22885		$571 + 730$
451	22170	$a_{1g}(3e_g \text{ MO TiO}_2)$	571
463	21600		$427 + 571 + 730$
522	19155		$427 + 571$
543	18415	$a_{1g}(e_g \text{ Ti}_{\text{VI}}^{3+})$	
574	17420		
667	14995		$427 + 2 \times 730$
688	14535		$571 + 2 \times 427$
709	14105		$427 + 571$
730	13700		571
739	13530		427
763	13105	$b_{1g}(e_g \text{ Ti}_{\text{VI}}^{3+})$	

Note: Bands of pure electron transitions are set off in bold.

not split normally. According to these suggestions, two bands of intracenter excitation corresponding to an electron transition from level t_{2g} to levels a_{1g} and b_{1g} of a $\text{Ti}_{\text{IV}}^{3+}$ ion should be expected in the luminescence excitation spectrum 820 nm of $\text{Ti}_{\text{IV}}^{3+}$ ions in rutile. However, four absorption bands occur in the experimental luminescence excitation spectrum, and each band has a fine structure (Fig. 4). It is reasonable to suggest that two additional short-wave excitation bands are induced by the $3e_g$ rutile molecular orbital comprising Ti^{4+} 3d-orbitals (69%) and oxygen orbitals (31%) (Tossel and Vanghan, 1974) and located in the conductance zone of the mineral. It is natural to expect that both level $3e_g$ pertaining mainly to the $\text{Ti}_{\text{VI}}^{4+}$ ion and level e_g of $\text{Ti}_{\text{IV}}^{3+}$ will split by low-symmetrical crystal-field components into two sublevels. The passing of an electron on these sublevels from the t_{2g} level of the $\text{Ti}_{\text{IV}}^{3+}$ main state results in appearance of two additional short-wave absorption bands at 400 and 450 nm in the luminescence excitation spectra of rutile. The pattern of the luminescence excitation spectrum 820 nm of implanted but not annealed rutile (Fig. 4, curve *a*) confirms this suggestion. Two additional short-wave excitation bands at 400 and 450 nm almost disappeared in this spectrum

owing to spreading of the energy levels of molecular orbitals of the crystal by its amorphization. In this case, bands of intracenter $\text{Ti}_{\text{IV}}^{3+}$ luminescence excitation in the regions 550 and 700 nm were retained and even reinforced, indicating their belonging to local, discrete centers, a number of which increased during implantation irradiation. The postimplantation annealing, recovering the rutile structure, reclaims excitation bands in the regions 400 and 450 nm (Fig. 4, curve *b*). The location of absorption bands in the luminescence excitation spectra of rutile, their component structure, and interpretation are listed in Table 2. As is known, the contribution of an atomic bond to the structure of rutile is rather great (Tossel and Vangham, 1974) and predetermines intense electron-vibration interaction and, hence, the occurrence of numerous vibrational repetitions of bands in the spectra. This explains the fine structure of the luminescence excitation bands and luminescence bands. Both simple (427, 571, and 730 cm^{-1}) and combination (composite) frequencies that cause vibrational repetition of purely electron transition are clearly traced in the excitation spectra. The absorption bands of purely electron transitions taken as head long-wave bands in each of four groups of excitation bands and the respective electron transitions are indicated in Table 2. The averaged energy of two electron transition from level t_{2g} to sublevels a_{1g} and b_{1g} in $\text{Ti}_{\text{IV}}^{3+}$ ions determines $10Dq = 15260 \text{ cm}^{-1}$ (Table 2).

Hence, crystal-field parameter Dq in the $\text{Ti}_{\text{VI}}^{3+}$ site in rutile equals 1526 cm^{-1} and is uncommonly low for trivalent titanium. However, this is explained easily by an elevated percentage of atomic bonds in rutile, which reduces formal ion charges in mineral structure, whereas parameter Dq comes from the model of point charges and decreases as these charges drop. It should be noted that the value $10Dq = E(3e_g) - E(2t_{2g}) = 2.1 \text{ eV}$ (16940 cm^{-1}) for $\text{Ti}_{\text{VI}}^{4+}$ ion in rutile is significantly lower than the value of $22000\text{--}23000 \text{ cm}^{-1}$ expected from the model of point charges (Tossel and Vangham, 1974) likely because of the same reason of an elevated share of atomic bonds.

In light of interpretation of absorption bands in luminescence excitation spectra of rutile, the scheme of electron levels of rutile energy has been improved and the energy levels of impurity ions of trivalent titanium in octahedral coordination have been shown therein (Fig. 1). The consideration of this scheme demonstrates the following. The split value of the $3e_g$ -orbital of Ti^{4+} ions occupying slightly oblong octahedral sites is 0.40 eV (3226 cm^{-1}). At the same time, a similar level e_g of $\text{Ti}_{\text{VI}}^{4+}$ ion is split by 0.535 eV (4135 cm^{-1}), which is 34% higher. Thus, Ti^{4+} and Ti^{3+} ions occupy different octahedral sites in the rutile structure. Ions of quadrivalent titanium occupy regular, slightly elongate octahe-

drons. One more type of octahedrons, which usually remains vacant, is established in the rutile structure. Although the average distance from the center of such an octahedron to ligands (0.2038 nm) is somewhat greater than in a regular octahedron (0.1958 nm), the former is very strongly distorted (flattened) along the Z axis (two distances by 0.1663 nm and four distances by 0.2226 nm in the plane of the x and y axes). The Z axis in these octahedrons is very close to $[110]$ and $[\bar{1}\bar{1}0]$ directions. The symmetry of this octahedron is $C_{2h}(C_2/m)$. These strongly flattened monoclinic distorted octahedrons are occupied with Ti^{3+} ions in rutile, which explains the great splitting of the e_g -orbital set therein.

The proposed scheme of levels explains the nature of coloration of doped and annealed samples of synthetic rutile. According to the luminescence data, reduction of part of the titanium to the trivalent state occurs during implantation under an excess of uncoupled electrons. Ions of trivalent titanium occupy vacant octahedral sites in the rutile structure and play the role of charge compensators during occupation of octahedral sites of Ti^{4+} ions by bivalent cobalt ions. Thus, the role of cobalt ions implanted into rutile for greenish and reddish brown coloration of irradiated mineral is indirect. Cobalt is a regulator that prevents oxidation and disappearance of trivalent titanium ions under annealing of doped rutile. Electron transition with charge transfer from ligand to metal $6t_{1u} \rightarrow t_{2g} (Ti_{VI}^{3+})$ with energy 2.89 eV (Fig. 1) gives birth to the absorption band 430 nm, which causes coloration of implanted rutile. This broad and strong absorption band is polarized. The direction of prevailing polarization is controlled by direction of charge transfer, which is determined by the direction of the shortest ligand-metal distance and the direction of greater overlapping of metal and ligand orbitals. This direction appears to be axis Z of octahedrons, which are occupied with ions of trivalent titanium, because octahedral sites of the rutile structure are strongly flattened along this axis. Therefore, the above absorption band has prevalent polarization $E \perp C$. In the absorption spectra of rutile $\{001\}$ plates, the polarization is stronger than in similar optical spectra of $\{100\}$ plates. According to the degree of compression of Ti^{3+} octahedrons, the above-mentioned electron transition is stronger in $\{001\}$ plates and weaker in $\{100\}$ plates, thus explaining different coloration of these plates. Thus, appearance of the band at 430 nm in the optical absorption spectra of rutile should be explained by increasing concentration of Ti_{VI}^{3+} . Reduction of titanium to trivalent state occurs in the course of implantation under an excess of uncoupled electrons. The newly formed ions of trivalent titanium occupy vacant octahedral sites in the rutile structure and play the role of charge compensators during occu-

pation of octahedral sites of Ti^{4+} ions by bivalent cobalt ions. All the described phenomena take place in the process of ion implantation and postimplantation annealing.

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