Neutron-Induced Molecular Defect O_2^- in Beryllium Orthogermanate

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Abstract—Be_2GeO_4 polycrystalline samples preliminarily irradiated by fast neutrons ($E \sim 1$ MeV, $\Phi = 4.5 \times 10^{17}$ cm^{-2}) were studied by photoluminescence spectroscopy using synchrotron radiation pulses for excitation. The neutron-induced luminescence band observed at 1.7 eV in the spectra of the irradiated samples is assigned to the radiative relaxation of a molecular ion O_2^-. The luminescence of these defects in the Be_2GeO_4 structure is effectively excited by 4.7- and 5.2-eV photons. At low temperatures (10 K), the profiles of the photoluminescence and excitation bands have a fine structure characteristic of electron–vibration interactions. The vibration frequencies for the ground state ($\nu_1 = 161$ cm^{-1}) and two excited states ($\nu_2 = 672$ cm^{-1} and $\nu_3 = 887$–1451 cm^{-1}) were measured. Potential curves of the energy states of the O_2^- center are constructed in terms of the Morse model using the experimental data. The optical spectrum fine structure is shown to be predominantly due to intrinsic vibrations of the molecular defect.

1. INTRODUCTION

The demands of the modern nuclear power engineering and radiation-resistant materials science, as well as the development of the element basis of electron-optic apparatuses and systems operating in intense radiation fields, make it important to study the properties and energy structure of radiation defects in solid materials. To date, radiation defects induced by high-energy radiations in alkali halide crystals (AHCs) have been studied in sufficient detail [1]. Studying materials based on simple oxides (BeO, MgO, Al_2O_3, SiO_2) has shown that the processes of generation and the behavior of radiation defects in these materials exhibit more complex character [1, 2]. A variety of types of structural damage and mechanisms of defect formation and the complexity of their identification do not allow the complete description of specific point defects in the complex oxides.

Point defects in irradiated simple wide-band-gap oxides are predominantly due to the occurrence of vacancies on both cation and anion sublattices. In this case, the oxygen atoms shifted from the equilibrium positions exhibit a pronounced tendency toward the formation of complex interstitial defects, such as O_2^-, O_2^+, O_2^0, O_3^-, and O_2^{3-} [2–4]. Among defects of this type, the molecular ion O_2^- is of special interest. Due to its specific luminescent optical properties, this center may be a suitable model for studying the interaction between the defect and the host matrix and for studying intramolecular electronic–vibrational optical transitions.

The luminescent properties of the O_2^- molecular ion have been studied in detail in AHCs grown in an oxygen atmosphere, for which this defect was an impurity [5–7]. Radiation-induced defects such as the interstitial oxygen form effectively in ion-implanted crystals, glasses, and thin SiO_2 films [8, 9]. In structures more complex in composition, e.g., in binary oxides, the properties of the O_2^- center remain poorly understood. In this work, we study the properties of radiation O_2^- centers in beryllium orthogermanate. The complex oxide Be_2GeO_4 is a wide-band-gap insulator crystallizing in the phenacite structure (Be_2SiO_4) [10]. These compounds are crystallochemical analogs and belong to the nesosilicate class (germanates). The crystal lattice of these materials consists of $[SiO_4/GeO_4]$ or $[BeO_4]$ tetrahedra, which are bound to each other and form chains oriented along the principal crystallographic axis C_3. The chains form voids in the form of wide channels ~4.5 Å in diameter [11]. A specific feature of phenacite-structure crystals is that the $[SiO_4]$ tetrahedra (or $[GeO_4]$ in the case of Be_2GeO_4) are separated, i.e., they do not touch each other. All oxygen atoms on the phenacite lattice are three-coordinated, and each of them is shared by three tetrahedra, namely, two $[BeO_4]$ and one $[Si(Ge)O_4]$.
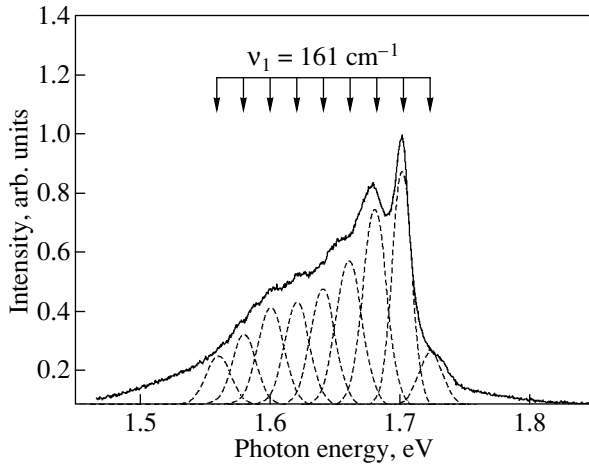
Fig. 1. Photoluminescence spectrum of the O_2^- molecular ion at $T = 10$ K excited in the band at 5.27 eV. Dashed lines show the spectrum expansion into Gaussians. Arrows indicate the rotational sublevels of the O_2^- molecular ion.

Fig. 2. Luminescence excitation spectrum of the band at 1.7 eV in the O_2^- molecular ion. Dashed lines show the spectrum expansion into two Gaussians with maxima at 4.7 and 5.2 eV (without allowance for the fine structure). Arrows indicate the vibrational structure of these two excitation bands. The expansion of the spectrum fine structure into Gaussians is shown only for the 5.2-eV band.

The results of studying radiation defects in $BeSiO_4$ single crystals and polycrystals irradiated by neutrons or protons have shown that this class of materials exhibits a fairly high radiation resistance [12–18]. It has been established that, in $BeSiO_4$ crystals irradiated by high-energy particles, radiation-induced defects are individual oxygen vacancies and oxygen-vacancy complexes. These facts suggest that the appearance and aggregation of shifted oxygen atoms is possible. However, phenacite-structure crystals have not been systematically studied in this direction.

The aim of this work is to study the luminescence characteristics and energy spectrum of the molecular oxygen centers generated by neutron irradiation in the germanate phenacite Be_2GeO_4.

2. EXPERIMENTAL

We studied Be_2GeO_4 polycrystalline samples prepared by high-temperature solid-phase synthesis. The samples were irradiated by fast neutrons (energy $E \sim 1$ MeV, flux $\Phi = 4.5 \times 10^{17}$ cm^{-2}) in a channel of the IBR-30 pulsed nuclear reactor (Joint Institute for Nuclear Research, Dubna).

The photoluminescence (PL) and excitation spectra were measured at temperatures of 10 and 300 K under selective excitation by 4- to 10-eV photons. The PL spectra and PL-excitation spectra were measured on the SUPERLUMI station (the HASYLAB laboratory, DESY, Hamburg) using synchrotron-radiation pulses [19]. For excitation in the range 4–10 eV, we used a 2-m vacuum monochromator. The PL-excitation spectra were normalized to the same number of photons incident on the sample. The PL spectra in the range 1.45–1.85 eV were analyzed using an ARC Spectra Pro-308i monochromator and an R 6358P photomultiplier.
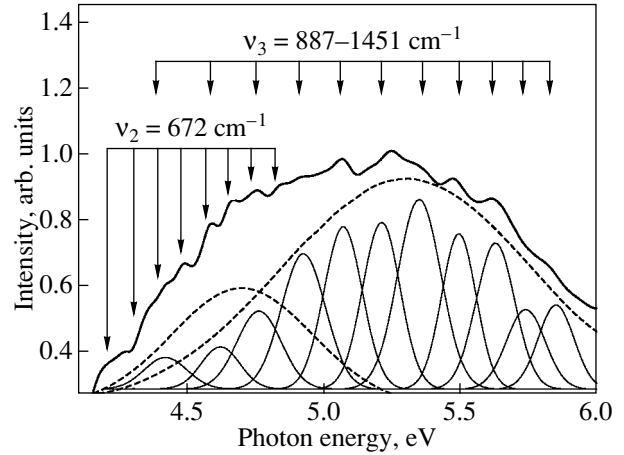
3. RESULTS AND DISCUSSION

3.1. Luminescence and Excitation Spectra

In a neutron-irradiated Be_2GeO_4 crystal, a red luminescence is observed in the spectral range 1.55–1.75 eV. It decays within several microseconds after the synchrotron-radiation pulse has ended. At room temperature, the PL spectrum contains a band with a maximum at 1.7 eV (the full width at half-maximum (FWHM) is 0.2 eV). At low temperatures ($T = 10$ K), the PL spectrum consists of a comparatively narrow intense line at 1.7 eV and several less intense lines located on the low-energy side (Fig. 1). The decomposition of the PL spectrum into Gaussian components revealed nine narrow (~ 18-meV-wide) equidistant lines. The average spacing between these lines is $\Delta E \approx 20$ meV. It is likely that the intense maximum at 1.7 eV is the principal line and other (less intense) lines are its vibrational replicas.

The PL at 1.7 eV is strong when excited by photons with energy $E_{exc} = 5.27$ eV and is very weak when excited in the fundamental-absorption range or above (7.35 and 27.5 eV). This PL occurs after neutron irradiation of Be_2GeO_4 and is excited in the transparent region of this crystal (4.0–6.0 eV); therefore, it can be interpreted as the intracenter PL of the radiation defects.

In the PL excitation spectra at 1.7 eV measured over the temperature range 10–300 K, we may separate two broad bands with maxima at 4.7 eV (FWHW = 0.45 eV) and 5.2 eV (FWHM = 0.75 eV). At low temperatures ($T = 10$ K), these excitation bands have a fine structure (Fig. 2), as is the case with the PL spectra. By decomposing the 4.7- and 5.2-eV bands of the low-temperature excitation spectra into Gaussians, their fine-structure parameters were obtained.

The observed structure of the low-temperature PL and excitation spectra is characteristic of the electron–vibration interactions in the luminescence center. It can be seen in Figs. 1 and 2 that the frequencies of the ground and excited states differ substantially. Using the spacings between the fine-structure lines, we determined the average vibration frequencies of the luminescence center. The average frequency ν_1 for the defect ground state is found to be 161 cm^{-1}. The excited states are characterized by vibrational frequencies of 672 cm^{-1} (ν_2) in the band at 4.7 eV and 887–1451 cm^{-1} (ν_3) in the band at 5.2 eV. The characteristic feature of the electronic–vibrational structure of the excitation spectrum is a regular variation in the frequency ν_3 of the 5.2-eV band, which is a manifestation of anharmonicity of the luminescence-center vibrations. It should be noted that the peculiarities of the PL and excitation spectra observed in the neutron-irradiated Be$_2$GeO$_4$ samples are typical of defect centers of the molecular type [3].

3.2. Radiation Damage

To identify the nature of the luminescence centers, let us consider the specific features of the interaction between fast neutrons and the Be$_2$GeO$_4$ crystal lattice. We will use the results of experimental studies of neutron-irradiated Be$_2$SiO$_4$ crystals reported in [12–18].

It has been established that, in neutron-irradiated Be$_2$SiO$_4$ crystals, oxygen vacancies are generated in the form of paramagnetic E' centers [14–17]. At sufficiently high dozes ($\Phi > 6 \times 10^{17}$ cm^{-2}), oxygen-vacancy complexes arise in the silicate phenacite, which were identified as oxygen divacancies [12]. Since irradiation by high-energy particles commonly creates vacancy–interstitial pairs, there should be not only vacancies but also shifted atoms. In silicates, the radiation defects analogous to shifted oxygen atoms can be peroxide radicals ($\equiv$Si–O–O$^\bullet$) and interstitial neutral O$_2$ and negatively charged O$_2^-$ molecules. The variation in the oxygen structural and energy state and the formation of O–O molecular groups in neutron-irradiated Be$_2$SiO$_4$ crystals are supported by x-ray photoelectron spectroscopy (XPS) data [13].

To determine the character of the structural damage in Be$_2$GeO$_4$, we calculated the probabilities of the interactions of fast ($\sim$ 1-MeV) neutrons with the nuclei of the Be, Ge, and O atoms that form the germanate phenacite.

Estimations performed using the method described in [20] show that, in Be$_2$GeO$_4$ crystals irradiated with neutrons, the cross sections of atomic displacements are largest for beryllium ($\sigma \sim 0.997$ cm^2) and oxygen ($\sigma \sim 0.991$ cm^2) atoms, whereas the cross section for germanium atoms is approximately 30% smaller and is $\sigma \sim 0.693$ cm^2 (the calculations are carried out to within a certain constant). Note that we obtained similar estimates for the atomic shifts in the silicate Be$_2$SiO$_4$. In

the latter case, the calculated results and the available experimental XPS data [13] show that fast neutrons are most likely to cause an impact displacement of oxygen atoms in the silicate phenacite Be$_2$SiO$_4$. According to the XPS data, the beryllium electronic states in the silicate phenacite do not exhibit radiation-induced variations, which is explained by the fact that light beryllium atoms again occupy regular lattice sites after the radiation exposure has ceased.

Thus, since there is crystallochemical similarity between Be$_2$GeO$_4$ and Be$_2$SiO$_4$, we may expect that it will be the oxygen sublattice that will suffer radiation damage in the Be$_2$GeO$_4$ crystalline structure under neutron irradiation. In this case, the oxygen atoms that are shifted into interstitial positions may form both neutral O$_2$ and negatively charged O$_2^-$ molecules possessing luminescence properties. It should be noted that the formation and stabilization of $\equiv$Si–O–O$^\bullet$ peroxide radicals in crystals with a phenacite structure is unlikely, since these defects can form only if two beryllium vacancies appear simultaneously in neighboring crystallographic positions.

3.3. The Nature of the Luminescence Center

To establish the nature of the revealed neutron-induced center in the crystalline Be$_2$GeO$_4$, we consider the optical properties of the most probable molecular defects (O$_2$ and O$_2^-$).

The PL properties of a the neutral oxygen molecule O$_2$ have been extensively studied in gaseous and liquid media [21, 22]. There are data on the PL of an interstitial O$_2$ molecule in irradiated and oxygen-enriched samples of glassy or crystalline silicon dioxide [23, 24]. The O$_2$-molecule energy levels involved in the PL are the $X^3\Sigma_g^-$ ground triplet and two excited $a^1\Delta_g$ and $b^1\Sigma_g^-$ singlets. It was shown in [21–24] that the positions of the maxima of the PL and excitation bands of the molecular oxygen O$_2$ are only weakly dependent on its local surroundings and are practically identical for gaseous and condensed media. In the gas phase, the PL of the center studied is observed at 762, 1269, and 1908 nm (E_{em} = 1.62, 0.97, and 0.65 eV, respectively) [22]. The probability of the first radiative transition (1.62 eV) is very low, and its detection is hampered due to the low PL quantum yield. In irradiated samples of glassy and crystalline SiO$_2$, this O$_2$-center PL band is not observed even at liquid-helium temperature [24].

The excitation and PL of the O$_2^-$ molecular ion occur through the electron transition between the $X^2\Pi_g$ ground state (electron configuration $\sigma_g^2\pi_u^4\pi_g^3$) and the $A^2\Pi_u$ excited state (configuration $\sigma_g^2\pi_u^4\pi_g^4$). The PL and excitation bands exhibit a line structure due to the intramolecular electron–vibration interactions of the

O_2^- center. According to the potential-energy curves presented in [7] for the ground and excited states of the O_2^- impurity defect in the NaCl crystal, the excitation and PL energy maxima are located at 5.1 and 2.0 eV, respectively.

Thus, from comparing the spectroscopic characteristics of the PL center revealed in the neutron-irradiated Be_2GeO_4 ($E_{em} = 1.7$ eV, $E_{exc} = 4.7$ and 5.2 eV) with those characteristic of the neutral O_2 ($E_{em} = 0.97$ eV, $E_{exc} = 1.62$ eV) [24] and charged O_2^- ($E_{em} = 2.0$ eV, $E_{exc} = 5.1$ eV) molecules, it follows that the experimental PL and excitation spectra of beryllium orthogermanate correspond to the O_2^- defect.

The conclusion that the O_2^- defect forms in Be_2GeO_4 agrees well with the results from [12, 16] where paramagnetic O_2^- molecular ions were revealed in a neutron-irradiated Be_2SiO_4 crystal using the EPR method. An analysis of the angular dependence of the g factor for the paramagnetic O_2^- center showed that this center exhibits axial local symmetry and that the defect axis coincides with the principal C_3 axis of the crystal. Since there is a crystallochemical analogy between Be_2SiO_4 and Be_2GeO_4 crystals, we can assume that the O_2^- luminescence center in the beryllium orthogermanate crystal is most likely located in the channels extended along the C_3 axis in this crystal. This allows us to use the quasi-molecular approach in analyzing the peculiarities of the energy structure of this defect.

3.4. Energy Structure of the O_2^- Center

Calculations of the electronic states of the diatomic molecule O_2^- located in vacuum or in an array of point charges modeling an ionic fcc crystal have shown [25] that, along with the $A^2\Pi_u$ excited state, there is another stable excited state, $a^4\Sigma_u^-$. This conclusion correlates with the presence of two bands with maxima at 4.7 and 5.2 eV in the PL excitation spectrum of Be_2GeO_4 (Fig. 2). In this work, we estimate the energy-structure parameters of the O_2^- ion in Be_2GeO_4 using the experimental spectroscopy data and the Morse model potential [26, 27]

$$U(r - r_0) = D[1 - \exp(\beta(r - r_0))]^2. \quad (1)$$

Here, r_0 is the equilibrium internuclear distance, D is the dissociation energy (in our case, $D = 4.083$ eV [23]), β is a parameter defined as

$$\beta = \nu_0 \sqrt{\frac{8\pi^3 c \mu}{Dh}}, \quad (2)$$

where ν_0 is the vibration frequency for the lower level, μ is the reduced mass, c is velocity of light in free space, h is the Planck constant.

Using the Morse potential and the above values of the intrinsic vibration frequencies of the O_2^--center in Be_2GeO_4, we can calculate the energy-structure parameters of this molecular ion. It follows from the experimental data (Fig. 2) that the first excited state of the O_2^- ion (excitation band at 4.7 eV) is characterized by a frequency $\nu_2 = 672$ cm^{-1}, from which we can find the potential-energy curve. Constructing the potential-energy curve for the second excited state (excitation band at 5.2 eV) is a more complicated task due to regular variations in the ν_3 value in the range 887–1451 cm^{-1} caused by vibration anharmonicity. The parameters of the second excited state (the initial vibration frequency ν_0 at the lower sublevel, the anharmonicity parameter ν_x) can be found in the Morse model using the expressions for neighboring level energies

$$E_V - E_{V-1} = h\nu_0 \left(1 - \frac{V}{V_{max}}\right) \quad (3)$$

and the maximum number of the vibrational sublevels V_{max} of the energy term with the initial frequency ν_0

$$V_{max} = \frac{h\nu_0}{2h\nu_x}. \quad (4)$$

The values of the difference ($E_V - E_{V-1}$) for the second excited state in expression (3) are found using the experimental sequence of the intervals between neighboring peaks of the fine structure of the PL excitation spectrum in Be_2GeO_4. Extrapolating the difference in Eq. (3) to $V = 0$, we determine the vibrational frequency of the lower sublevel $\nu_0 = 1612.2$ cm^{-1} and the maximum number of the vibrational sublevels $V_{max} = 27$. Substituting these values into expression (4), we find the anharmonicity parameter $\nu_x = 29$ cm^{-1} ($h\nu_x = 0.003515$ eV).

Based on these calculations, we constructed the potential curves for the energy states of the O_2^- molecular ion in the Be_2GeO_4 lattice (Fig. 3). From these curves, it follows that, in the germanate phenacite, the equilibrium distance between the oxygen atoms in the O_2^- center is ~ 1.25 Å for the ground state and 1.50 and 1.75 Å for the first and second excited states, respectively.

The differences between the calculated equilibrium distances and the anharmonicity parameter for the molecular defect and the respective quantities for the free O_2^- ion ($r_e = 1.38$ Å, $h\nu_x = 0.0015$ eV [28]) can be assigned to the defect–matrix interaction. In this connection, it should be noted that, although the Morse potential is most appropriate for analyzing intramolecular interactions [26, 27], the approach used in this study makes it possible to include the effect of the Be_2GeO_4 matrix on these interactions. To reveal the specific features of the effect of the crystal lattice on the O_2^- center, it is necessary to consider the electronic–vibrational transitions characteristic of this defect.

3.5. Electron–Vibration Interactions

The electron–vibration interactions manifest itself in both the ground and excited states of the O_2 center. The measured values of the frequencies ν_2 (672 cm^{-1}) and ν_3 (887–1451 cm^{-1}) of the defect center in Be_2GeO_4 are close in order of magnitude to the corresponding frequencies of the totally symmetrical vibrations of the free diatomic molecule O_2^- [28]. This means that, in the neutron-irradiated Be_2GeO_4, the electronic states interact predominantly with local vibrations of the molecular defect rather than with phonon modes of the crystal lattice. However, the fact that the value of the frequency ν_1(161 cm^{-1}) obtained from the PL spectra of Be_2GeO_4 is lower indicates that the electron–vibration interaction in the process of radiative relaxation is different in character.

Analogous low-frequency vibrations were also observed earlier in the PL spectra of the O_2 ion in AHCs, wherein this ion occupies the halogen position and is significantly influenced by the crystal lattice [6]. The complex substructure of the PL spectra, which can be resolved for each of the zero-phonon lines at liquid-helium temperatures, is due to the interaction of the luminescence center with the low-frequency vibrations of the AHC lattice (at frequencies of 120 cm^{-1} or higher) and with the O_2^- ion libration (at frequencies below 60 cm^{-1}). However, it is most likely that, in the Be_2GeO_4 structure, this center is located in hollow channels oriented parallel to the C_3 axis. Thus, the vibrational structure of the O_2-center PL spectra in Be_2GeO_4 reflects the presence of predominantly intramolecular interactions. In other words, the O_2 defect center can be considered, in a certain sense, an almost free ion whose intrinsic vibrations are disturbed by the interaction with the Be_2GeO_4 lattice.

This conclusion agrees well with the results from analyzing the O_2-center energy structure (Fig. 3), according to which the equilibrium interatomic O–O distances in the ground and excited states, as well as the anharmonicity parameter, differ from those found from the potential-energy curves for the free O_2^- molecule [28]. Moreover, we can assume that the low-frequency vibrational structure of the Be_2GeO_4 PL spectrum resolved at low temperatures is related to the low-energy rotational modes of the molecular O_2 ion rather than to the electron–phonon interaction.

Thus, we can conclude that the optical transitions to excited states of the O_2 center in the neutron-irradiated Be_2GeO_4 involve the totally symmetrical vibrations characteristic of the diatomic molecule, whereas the radiative relaxation of this defect involves the rotational sublevels.
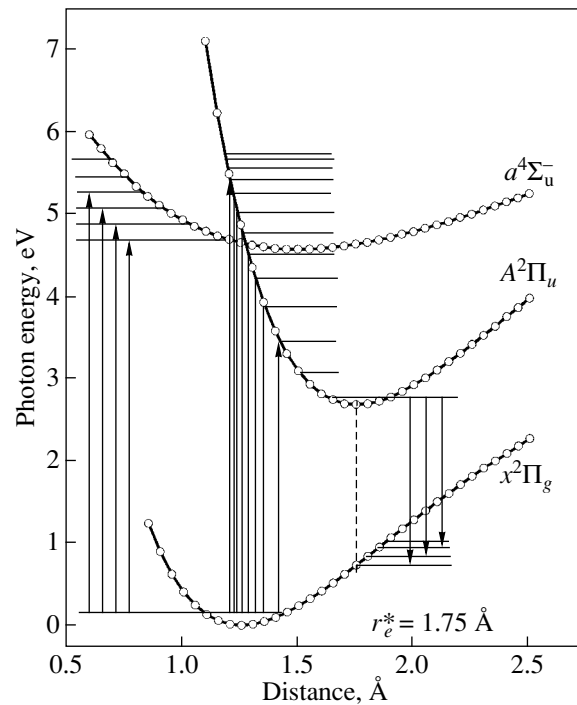

Fig. 3. Electronic terms and a diagram of optical transitions constructed for the O_2^- molecular ion in Be_2GeO_4 using the Morse model potential and the experimental values of the optical-transition energies and vibrational–rotational frequencies. Horizontal lines show the vibrational and rotational sublevels.

4. CONCLUSIONS

(i) Point-defect luminescence has been revealed in the polycrystalline beryllium orthogermanate irradiated by fast neutrons. The defect has been identified as the molecular oxygen ion O_2^-. This luminescence center is most likely located in structural channels oriented along the principal crystallographic axis of Be_2GeO_4.

(ii) Based on the spectroscopic data and calculations in terms of the quasi-molecular approach, we have established some specific features of the O_2-center energy structure. The differences observed between the energy terms of this radiation defect and those of the free O_2^- molecule have been explained by the effect of the crystal lattice.

(iii) The analysis of the optical-spectrum structure has shown that the defect photoexcitation is accompanied by the interaction of the electronic states with the totally symmetrical local vibrations and that the radiative relaxation involves predominantly the rotational modes.

ACKNOWLEDGMENTS

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