

OPTICAL CENTERS AND THE INTERACTION OF Yb^{3+} IONS IN CUBIC FLUORITE CRYSTALS

Yu. K. VORON'KO, V. V. OSIKO, and I. A. SHCHERBAKOV

P. N. Lebedev Physics Institute, U.S.S.R. Academy of Sciences

Submitted August 13, 1968

Zh. Eksp. Teor. Fiz. 56, 151-160 (January, 1969)

The optical spectrum and lifetime of the excited ${}^2\text{F}_{5/2}$ level in $\text{CaF}_2 - \text{Yb}^{3+}$ crystals are investigated in a broad range of concentrations (0.01-30 wt.%) at the temperatures 300°, 77°, and 4.2°K. The ${}^2\text{F}_{7/2}$ and ${}^2\text{F}_{5/2}$ level schemes obtained taking Stark splitting into account are presented for centers of cubic symmetry and for the centers that determine the optical spectrum of $\text{CaF}_2 - \text{Yb}^{3+}$ at concentrations of 1 wt.% and higher. It is established that energy is transferred between Yb^{3+} ions in centers having different structures.

INTRODUCTION

ONE of the simplest energy level schemes among rare-earth ions belongs to Yb^{3+} ions, which have a ${}^2\text{F}_{7/2}$ ground level and a ${}^2\text{F}_{5/2}$ level that are separated by 10^4 cm^{-1} . The ytterbium ion is therefore a suitable object for investigations of optical centers and certain properties that are common to all rare-earth ions, such as energy transfer processes, quenching etc. The optical spectra of Yb^{3+} and CaF_2 have been investigated in^[1-3], where extensive data can be found. However, the results presented by different authors are not always in agreement. The large discrepancies that have not previously been accounted for pertain mainly to the interpretation of the absorption and luminescence spectra. It is therefore of interest 1) to investigate changes in the spectra depending on different conditions of crystal growth, for an identical activator concentration; and 2) to study the concentration dependences of the spectra for crystals grown under identical conditions. The first of these tasks has been accomplished to a considerable degree in^[4]. It should be noted, however, that all the hitherto published investigations of the optical spectra pertain to Yb^{3+} concentrations not exceeding 0.5 wt.%. The weak concentration quenching of Yb^{3+} in CaF_2 and the possibility of energy transfer from Yb^{3+} ions to several other ions (for example, in yttrium aluminum garnet (YAG) crystals with several different activators^[5]) make it of interest to investigate this system in a broad range of concentrations; such is the purpose of the present work.

CRYSTALS

The type I $\text{CaF}_2 - \text{Yb}^{3+}$ crystals were grown in a fluorinating atmosphere by the technique described in^[7]. The Yb^{3+} concentrations ranged from 0.01 to 30 wt.%.

APPARATUS AND EXPERIMENTAL TECHNIQUE

The absorption spectra were registered in the region 9100-9900 Å (the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition). The spectra were measured using a double-beam technique

with an SF-8 spectrophotometer at 300° and 77°K, and using a single-beam technique with a DFS-12 spectrometer at 300°, 77°, and 4.2°K. The luminescence spectra were registered with the DFS-12 spectrometer in the region 0.96-1.08 μ at 300° and 77°K. The crystals were excited with a 300-Wt incandescent lamp placed at a right angle to the viewing direction. The signals from the FEU-22 photomultiplier used as a detector were amplified and recorded automatically. The technique described in^[8] was used to measure the lifetimes, at 300° and 77°K, of individual luminescence lines discriminated by the DFS-12 spectrometer. For the purpose of reducing reabsorption the crystals having large Yb^{3+} concentrations (above 1 wt.%) were prepared in the form of 2.5-mm cubes. Through special studies performed to determine the maximum crystal size for which reabsorption still remains negligible and does not affect τ_{rad} it was shown that the selected sizes did not distort the results even for crystals having 30 wt.% Yb^{3+} .

ABSORPTION AND LUMINESCENCE SPECTRA. LIFETIMES

Figures 1 and 2 show concentration series of the absorption spectra at 4.2° and 77°K, respectively. Important changes are observed as the concentration is varied. Different lines become dominant, along with changes in the total number of lines, their intensities and widths.

Upon going from nitrogen to helium temperatures with a fixed Yb^{3+} concentration only the relative line intensities are found to change, while the number of lines remains unaltered. The only exception is found in the system of broad lines that is dominant beginning at concentrations of 3 wt.%; in this system the wavelengths 9846, 9860, and 9921 Å are "frozen out." The widths of the great majority of lines are strongly temperature-dependent; for example, the width of the 9685-Å line is 10 cm^{-1} at 77°K, but only 3 cm^{-1} at 4.2°K. The only prominent exception is the 9630-Å line, which exhibits a practically constant linewidth $\sim 1 \text{ cm}^{-1}$ in the temperature range 77-4.2°K. This line is also distinguished by the fact that it is the only spectral line observed by us throughout the entire in-

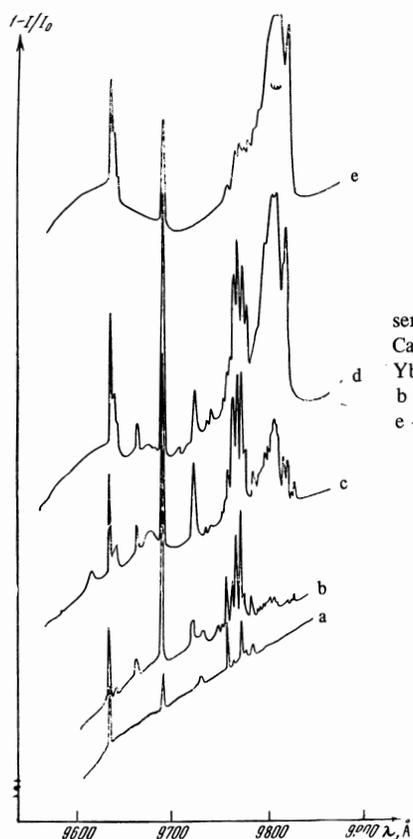


FIG. 1. Concentration series of absorption spectra of $\text{CaF}_2\text{-Yb}^{3+}$ crystals at 4.2°K . Yb^{3+} concentrations: a - 0.03, b - 0.1, c - 0.3, d - 1, e - 3 wt. %.

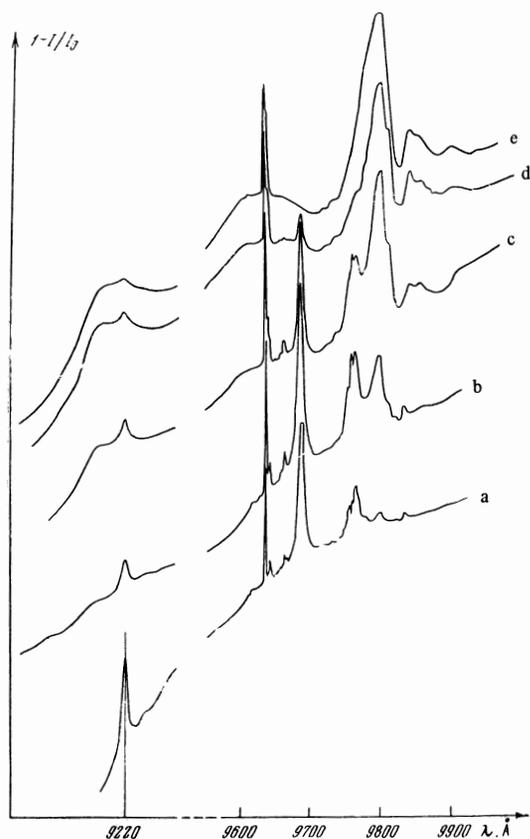


FIG. 2. Concentration series of absorption spectra of $\text{CaF}_2\text{-Yb}^{3+}$ crystals at 77°K . Yb^{3+} concentrations: a - 0.1, b - 0.3, c - 1, d - 3, e - 10 wt. %.

vestigated range of concentrations (0.01–30 wt. %). However, beginning at 1 wt. % it becomes complex and consists of at least two weakly resolved components.

Figure 3 shows the concentration series of luminescence spectra of the $\text{CaF}_2\text{-Yb}^{3+}$ crystals. Here, as in the absorption spectra, we observe marked concentration dependence. A comparison reveals that at low Yb^{3+} concentrations the luminescence spectra exhibit resonance character, except in the case of the $10270\text{-}\text{\AA}$ line. At high concentrations the long wavelength portion of the luminescence spectrum contains several broad lines, some of which represent transitions to excited components of the ${}^2\text{F}_{7/2}$ ground level. Other bands are not correlated with the absorption spectra.

The lifetimes of individual luminescence lines were measured at 300° and 77°K for different Yb^{3+} concentrations (Fig. 4, a and b). The 9630- and $10270\text{-}\text{\AA}$ lines were found to possess the longest values of τ_{rad} , which reached $12\ \mu\text{sec}$ at 77°K for low Yb^{3+} concentrations. With increasing Yb^{3+} concentration the lifetimes of these lines are shortened rapidly. All the other lines have approximately an identical lifetime $\sim 2\text{--}3\ \mu\text{sec}$ with weak concentration dependence. Figure 4 shows that the temperature dependence of τ_{rad} is affected strongly only in the region of the 9630- and $10270\text{-}\text{\AA}$ lines when we go from nitrogen to room temperature. The lifetimes of the other luminescence lines are only weakly temperature dependent.

DISCUSSION OF RESULTS

Yb^{3+} optical centers in CaF_2 crystals. By investigating the optical centers and lifetimes of $\text{CaF}_2\text{-Yb}^{3+}$ crystals in a broad range of concentrations we are enabled, in first approximation, to discriminate the systems of lines belonging to individual optical centers

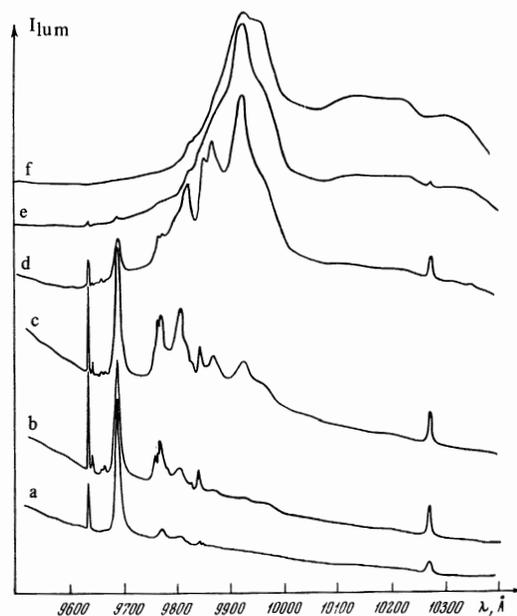


FIG. 3. Concentration series of luminescence spectra of $\text{CaF}_2\text{-Yb}^{3+}$ at 77°K . Yb^{3+} concentrations: a - 0.03, b - 0.1, c - 0.3, d - 1, e - 3, f - 10 wt. %.

or groups of centers, and also to arrive at conclusions regarding the transfer of excitation energy between these centers.

Let us consider the variations in the luminescence and absorption spectra having identical Yb³⁺ concentrations as the concentration is increased. With ~0.01 wt.% the absorption spectrum consists of only two lines, at 9220 and 9630 Å. For low Yb³⁺ concentrations these lines are characterized by identical behavior of their concentration curves (Fig. 4c) and according to^[9] they must both belong to centers of cubic symmetry. This conclusion is supported by the results obtained in^[4], where the optical spectra are compared with EPR spectra and it is shown that the 9630-Å line belongs to centers of cubic symmetry. The different linewidths of 9630 and 9220 Å evidently result from the fact that 9630 Å is a resonance line and is slightly broadened by interaction with lattice vibrations, whereas the 9220-Å line represents a transition to an excited component of the ²F_{5/2} level and can be broadened considerably by interaction with phonons.^[4]

In the luminescence spectra of the same crystals (CaF₂ - 0.01% Yb³⁺) we observed three lines—at 9630, 10195, and 10270 Å. The similar concentration dependences of the luminescence, along with the coincident magnitudes and concentration dependences of τ_{rad}, permit confident assignment of the 10270- and 9630-Å lines to a single type of optical centers, which is therefore the cubic type. The 10195-Å line could not be assigned with the same confidence. The intensity of this line is small, and although its concentration dependence was found to resemble that of the 9630- and 10270-Å lines we were unable to measure its lifetime. The line at 10195 Å can therefore be assigned only provisionally to centers of cubic symmetry. Figure 5a shows the level scheme of Yb³⁺ in the cubic field of the fluorite.

Our results, which were obtained using optical methods, coincide very accurately with the results given in^[10], where it was established by double electron-nuclear resonance that the Γ₈ - Γ₇ splitting of the ²F_{7/2} ground state in a cubic field is 604 ± 10 cm⁻¹, while the Γ₆ - Γ₇ splitting is 584 cm⁻¹. For Yb³⁺ concentrations beginning at 0.03 wt.% the absorption spectra include several lines whose intensity at first increases very rapidly as far as ~0.3%, after which the intensity begins to diminish.

Figure 4c shows the concentration dependence of the absorption coefficient for one of these lines (9685 Å).

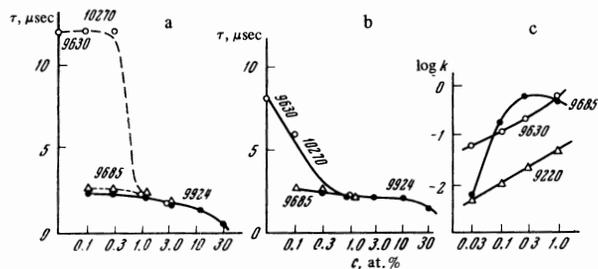


FIG. 4. Concentration dependence of the lifetime τ_{rad} and of the absorption coefficients: a - of τ_{rad} at 77°K different centers; b - the same at 300°K; c - of the absorption coefficients at 4.2°K.

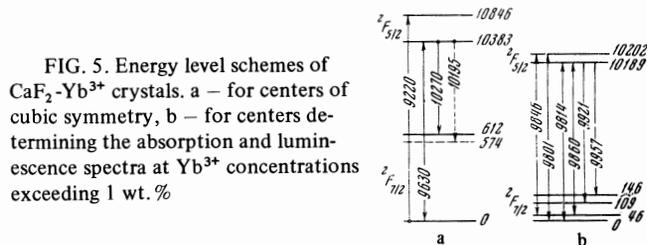


FIG. 5. Energy level schemes of CaF₂-Yb³⁺ crystals. a - for centers of cubic symmetry, b - for centers determining the absorption and luminescence spectra at Yb³⁺ concentrations exceeding 1 wt. %

In^[4] this strong resonance line is associated with centers of tetragonal symmetry. We assign to the same group a number of close resonance lines in the range 9750-9780 Å (Fig. 1). It should be noted that this strong group was not observed in^[4]; on the other hand, one of the strongest lines registered by the authors of^[4] and identified by them as a line at 9749 Å from a center of tetragonal symmetry T₂ is not present in our spectra. This essential difference between the spectra seems to be attributable to the fact that none of the methods of crystal growing used and described by the authors of^[4] can completely eliminate oxygen contamination, whereas our method of crystal growing in a measured fluorinating atmosphere^[7] yields oxygen-free crystals. The differences in the concentration dependences of lines in the region 9750-9785 Å at helium temperatures (when these lines are sufficiently well resolved, as seen in Fig. 1) suggest that these lines belong to different types of optical centers (apparently six or seven in number). The fact that the absorption spectra do not include excited components of these lines indicates substantial splitting of the lowest level in these centers. Nothing can be said concerning the character and symmetry of these centers without utilizing other methods of investigation.

Beginning at 0.3 wt.% Yb³⁺ the optical spectra of CaF₂ - Yb³⁺ reveal still another group of lines that determines the absorption and luminescence spectra at high concentrations. Above 3 wt.% the lines of this group are quite broad and are not resolved into narrower components at 4.2°K. However, in the case of lower concentrations (0.3-1 wt.%) at 4.2°K one band (9801-9814 Å) of this group is split into a series of narrow lines.

By comparing the absorption spectra at 77° and 4.2°K, and also by comparing the absorption and luminescence spectra at 77°K (Fig. 6) we learn that the groups of lines at 9846-9860 and 9921-9957 Å represent transitions from excited components of the ground states belonging to the corresponding groups of centers. Taking into account the different intensities in the ab-

Vibrational frequencies in the absorption and luminescence spectra of CaF₂ - Yb³⁺ crystals

Absorption spectrum, cm ⁻¹	Luminescence spectrum, cm ⁻¹
—	330
405	410
490	495
640	660

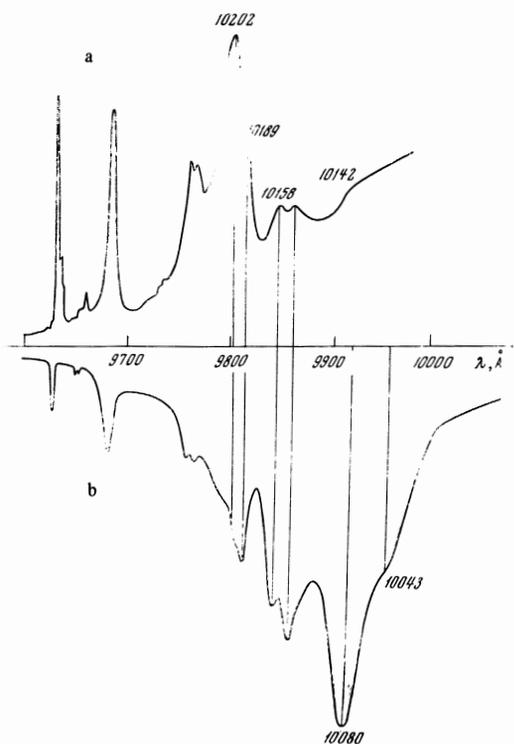


FIG. 6. Absorption and luminescence spectra of CaF_2 -1 wt. % Yb^{3+} at 77°K. a - absorption spectrum; b - luminescence spectrum.

sorption and luminescence spectra (Fig. 6), we can construct the level scheme of these centers as was done for Fig. 5b.

The spectra of fluorite crystals activated by Tr^{3+} , and particularly Yb^{3+} , are known to be characterized by a set of optical centers whose composition and relative numbers vary with the total Tr^{3+} concentration.^[9] At low concentrations of the rare-earth admixture there is a small number of centers, which vary considerably in structure, so that great differences of their optical properties appear. With increasing Tr^{3+} concentration there is a growing number of centers having different structures, but the differences between the structures becomes less and less significant. Consequently, at high Tr^{3+} concentrations the absorption and luminescence lines of different Tr^{3+} centers are grouped about energy levels that are determined by the average field of the impurity ions. The structure of the optical spectra no longer varies with the concentration, and the number of Stark components is the maximum number possible in the average field. This pattern is observed in the $\text{CaF}_2 - \text{Yb}^{3+}$ spectra. At $\sim 0.3\%$ Yb^{3+} the observed system of lines includes resonance lines in the region 9801–9814 Å.

Beginning at the 1% concentration the 9801–9814-Å band can no longer be resolved; all the lines in the band then appear to represent a single transition between a pair of Stark components. The excited levels for this system of centers fit easily into the level scheme of Fig. 5b. Figure 3 shows that for high Yb^{3+} concentrations at 77°K the bands having wavelengths that fit into the level scheme of Fig. 5b, in the lumi-

nescence spectra, are accompanied by other bands whose origin cannot be accounted for within the framework of the proposed level scheme. Exactly as in the case of the absorption spectra of Fig. 2, for high Yb^{3+} concentrations several bands cannot be described by the scheme of Fig. 5b. We have suggested that these lines are associated with an interaction between lattice vibrations and pure electronic transitions. One could then hardly expect complete correspondence between the vibrational spectra for absorption and luminescence, because these spectra result from different electronic states with possibly different potential curves. Nevertheless, the vibrational frequencies in the absorption and luminescence spectra, measured from the zeroth band (10200 cm^{-1}) of a pure electronic transition, are found to agree satisfactorily. The results are given in the table.

The concentration dependence of the cubic centers (Fig. 4c) merits a more detailed discussion. As was shown recently in^[9,11], independently of the fact that the rare-earth ions can be distributed statistically (uniformly) or can form clusters (nonuniform distribution), as the total ion concentration increases the cubic centers are replaced by centers of gradually increasing complexity. It was here assumed that in the case of the nonuniform distribution the system was in thermodynamic equilibrium. An experimental investigation of fluorite-neodymium crystals yielded results that agreed well with the theory; increasing neodymium concentration was accompanied by enhanced relative concentration of complex centers. However, studies of $\text{CaF}_2 - \text{Gd}^{3+}$ crystals^[12-14] and of $\text{CaF}_2 - \text{Eu}^{3+}$ crystals^[15] showed that, just as in the case of $\text{CaF}_2 - \text{Yb}^{3+}$, the concentration of cubic centers remains high even when the total ion concentration is very large.

The foregoing results suggest that there is considerable difference between the distribution of heavy and light rare-earth ions. The heavy ion distribution is of neither the uniform nor the nonuniform equilibrium type. It appears that fluorite crystals having these impurities are not in equilibrium. It is possible that Eu^{3+} , Gd^{3+} , Yb^{3+} , and interstitial F_i ions are imbedded in the fluorite lattice in the form of blocks, thus forming both microregions of ion clusters and regions where the impurity ions have been depleted so that the concentration of cubic centers is high.

Transfer of excitation energy between Yb^{3+} ions.

Figure 4, a and b, shows the concentration dependences of the lifetime τ_{rad} for different Yb^{3+} luminescence lines. For concentrations above 1 wt.% the values of τ_{rad} for the different types of centers practically coincide. It is thus indicated that in the given region excitation energy is exchanged efficiently between all centers, independently of their character or structure. An analysis of the spectra within a broad range of concentrations beginning with 1 wt.% shows that this energy exchange between ions does not result in the quenching of luminescence. We have not evaluated quantitatively the dependence of the luminescence yield on Yb^{3+} concentration. However, the given data show the occurrence of only slight Yb^{3+} quenching even at 3 wt.%. Therefore the analysis of the concentration dependences $\tau_{\text{rad}} = f(c)$ (Fig. 4, a and b) shows that

weak quenching of the luminescence of complex centers begins only at concentrations ~ 10 wt.%.

Figure 4, a and b, shows that efficient concentration quenching occurs only for cubic luminescence centers; this quenching effect is considerably stronger at room temperature than at nitrogen temperatures, and begins at very low concentrations (0.01–0.03 wt.%). At 77°K the quenching begins for 0.3 wt.%, because up to 0.3 wt.% Yb^{3+} the centers are widely separated and do not interact. At ~ 0.3 wt.% a considerable number of centers with a relatively short lifetime ($\sim 2 \mu\text{sec}$) appear; the interaction between these centers and cubic centers shortens the lifetime of the latter considerably. Above 1 wt.%, energy is exchanged efficiently between all centers. Consequently the quantum luminescence yield of centers possessing long lifetimes will diminish, since energy relaxation takes place at centers having short τ_{rad} . Herein lies the explanation of the fact that absorption lines of cubic centers which are observed throughout the entire concentration range 1–30 wt.% have practically vanished from the luminescence spectra beginning at 3 wt.%. The difference between the behavior of the concentration dependence of τ_{rad} at 77° and at 300°K is evidently accounted for by the thermal broadening of optical lines and the associated increased probability of a resonance interaction mechanism.

It should be noted, finally, that the lifetimes at 300°K are longer, by an amount exceeding the experimental error, than at 77°K for crystals having concentrations above 0.3 wt.%. No satisfactory explanation has been found for this effect, which also occurs in several other crystals that are activated by rare-earth ions.

In conclusion, the authors wish to thank M. V. Dmitruk for providing the investigated crystals, and V. A. Myzina for experimental assistance.

trosk, 13, 235 (1962) [Opt. Spectrosc. 13, 129 (1962)].

²W. Low, J. Chem. Phys. 37, 30 (1962).

³Z. J. Kiss, Phys. Rev. 127, 718 (1962).

⁴J. Kirton and S. D. McLaughlan, Phys. Rev. 155, 279 (1967).

⁵L. F. Johnson, J. E. Geusic, and L. G. Van Uitert, Appl. Phys. Lett. 8, 200 (1966).

⁶V. V. Osiko, Rost kristallov, Vol. 5, 373, 1965 [Growth of Crystals, Vol. 5B Consultants Bureau, New York, 1968, p. 163].

⁷Yu. K. Voron'ko, V. V. Osiko, V. T. Udovenchik, and M. M. Fursikov, Fiz. Tverd. Tela 7, 267 (1965) [Sov. Phys. Solid State 7, 204 (1965)].

⁸Yu. K. Voron'ko and V. V. Osiko, ZhETF Pis. Red. 5, 357 (1967) [JETP Lett. 5, 295 (1967)].

⁹V. V. Osiko, Fiz. Tverd. Tela 7, 1294 (1965) [Sov. Phys.-Solid State 7, 1047 (1965)].

¹⁰J. M. Baker, W. B. J. Blake, and G. M. Copland, Phys. Lett. 26A, 504 (1968).

¹¹V. V. Osiko, Neorganicheskie materialy (Inorganic Materials) 5, No. 3 (1969).

¹²F. Z. Gil'fanov, Zh. S. Dobkina, A. A. Stolov, and L. D. Livanova, Opt. Spektrosk. 20, 283 (1966) [Opt. Spectrosc. 20, 152 (1966)].

¹³F. Z. Gil'fanov, A. M. Leushin, and A. L. Stolov, Fiz. Tverd. Tela 9, 1357 (1967) [Sov. Phys.-Solid State 9, 1061 (1967)].

¹⁴F. Z. Gil'fanov, L. D. Livanova, and A. L. Stolov, Fiz. Tverd. Tela 9, 427 (1967) [Sov. Phys.-Solid State 9, 326 (1967)].

¹⁵B. P. Zakharchenya and I. B. Rusanov, Fiz. Tverd. Tela 8, 41 (1966) [Sov. Phys.-Solid State 8, 31 (1966)].

¹A. A. Kaplyanskiĭ and P. P. Feofilov, Opt. Spek-