

Instability of Monovalent Ions of Transitional Metals in Alkaline Earth Fluorides: CaF_2 and SrF_2 Activated by Co^{2+} or Ni^{2+}

A. V. Egranov^{a, b, *}, T. Yu. Sizova^a, and V. A. Kozlovskiy^a

^aVinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia

^bIrkutsk State University, Irkutsk, 664003 Russia

*e-mail: alegra@igc.irk.ru

Abstract—The ground state of monovalent ions of transitional metals in alkaline-earth fluorides is localized in the conduction band. It is shown by the example of monovalent Co and Ni ions in CaF_2 and SrF_2 crystals that this is responsible for the unstable state of these ions in cubic environments. A stable state is achieved by the monovalent ions shifting to off-center positions.

DOI: 10.3103/S1062873817090088

INTRODUCTION

In [1–4], we considered the instability of some divalent rare-earth (RE) ions characterized by the low third ionization potential. It was shown that their ground d^1 -state was localized in the conduction band, suggesting their instability in alkaline-earth fluorides (AEFs). Due to the Jahn–Teller effect, such instability leads to the formation of anion vacancies near divalent RE ions, reducing its ground state and making it stable in an AEF lattice. Because of the localization of the ground d^1 -state in the conduction band, the Jahn–Teller effect distorts the lattice more strongly than is usually observed upon localization of the degenerated d -state in the forbidden band.

Strong Jahn–Teller distortion, which results in considerable off-center shifts of impurity ions, is observed in AEFs activated by ions of transitional metals that are also characterized by degenerated d -ground states [5, 6].

In this work, we show that such instability is also typical of monovalent ions of transitional metals characterized by degenerated ground d -states. Estimates of the position of the ground state for all monovalent ions of transitional elements from Ti to Cu shows they are localized in the conduction band, resulting in their unstable state. Strong off-center Jahn–Teller distortion of some ions lowers their Madelung energy; this reduces the ground state of these ions relative to the conduction band, and their state is stabilized.

We studied the absorption, luminescence, and excitation spectra of the monovalent ions of Co^+ and Ni^+ in CaF_2 and SrF_2 crystals. We found that the absorption bands of these ions are associated with

charge transfer transitions from the conduction band to impurity ions, caused by an allowed $p \rightarrow d$ transition with an oscillation force almost two times stronger than of the intracenter $d \rightarrow d$ and $d \rightarrow s$ transitions of these ions. Analysis of the luminescence spectra of Co^+ ions in CaF_2 and SrF_2 crystals shows that the symmetry of the centers is clearly not cubic, and they probably occupy off-center positions in these crystals along with Ni^+ ions.

Below, we discuss the intensification of Jahn–Teller distortion, which in one case leads to the formation of anion vacancies near RE divalent ions, and in another to strong off-center shifts of the monovalent ions of transitional metals upon localization of their ground state in the conduction band.

EXPERIMENTAL

AEF crystals activated by transitional metals Co^{2+} and Ni^{2+} were grown from a melt under an inert atmosphere using the Stockbarger technique. Before being charged, the salts of transitional metals CoF_2 and NiF_2 were dried in vacuum. To prevent the formation of oxygen impurities, CdF_2 was added to each charge. Radiation coloring was performed using an X-ray tube with a Pd anode at 20 mA, 40 kV, and periods of irradiation no more 60 min long. The luminescence spectra were measured on a LS-55 luminescence spectrometer (PerkinElmer) equipped with an R928 photomultiplier tube. The absorption spectra were registered on a Lambda 950 UV/VIS/NIR spectrophotometer.

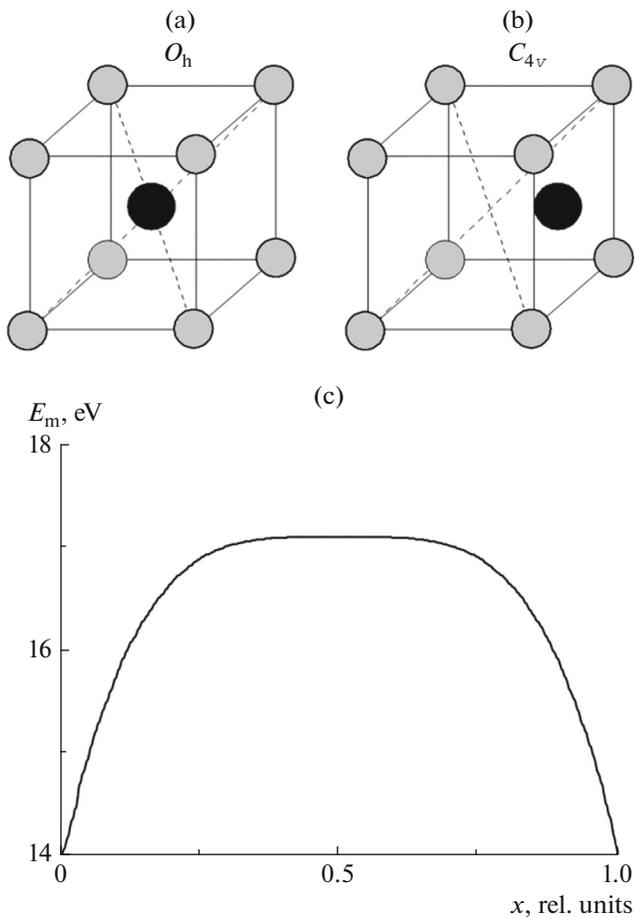


Fig. 1. Variation in Madelung energy E_m (c) when an impurity cation shifts from (a) a central position ($x = 0.5$) to (b) an off-center position toward $\langle 100 \rangle$; $x = 1$ corresponds to the distance between anions.

RESULTS AND DISCUSSION

Localization of the Ground State of Monovalent Ions

Most works on the localization of ions of transitional metals with different valences relative to the conduction band have been dedicated to alkali halide crystals [7, 8]. Rough estimates of the positions of the levels of monovalent ions of transitional metals from Ti^+ to Cu^+ in AEFs relative to the conduction band ($E_{\text{DC}} = -I + E_m + \Delta E_m$) shows that the levels of these ions are localized in the latter. This is because ionization potential I of the monovalent ions (which varies from 13.58 eV for Ti^+ to 20.2924 eV for Cu^+) is low, relative to Madelung energy E_m of the AEFs (21.67, 20.79, and 19.61 eV for CaF_2 , SrF_2 , and BaF_2 , respectively). Correction ΔE_m for the Madelung energy associated with the sizes of impurity ions will also increase this energy, since monovalent transitional metals are characterized by ionic radii smaller than those of diva-

lent alkaline earth metals. It should be noted that in alkali halide crystals, the Madelung energy is nearly half that in alkaline earth metals, resulting in the stable state of monovalent ions of transitional metals in the regular lattice nodes of these crystals [8].

Localization of the ground state in a conduction band results in the configuration instability of monovalent ions of transitional metals in a cubic environment. It is known [9–13] that Ni^+ ions are stable in off-center positions in the lattices of AEFs with symmetry C_{4v} . An estimated variation in the Madelung energy upon the distortion of an impurity cation toward $\langle 100 \rangle$ from center is shown in Fig. 1. We can see that with a substantial off-center shift, the Madelung energy falls considerably, reducing the ground state of the impurity cation relative to the conduction band and producing a stable configuration of this ion. It was shown in [1–4] that this reduction in the ground state relative to the conduction band results from the formation of anion vacancies near RE ions. The off-center shift of an ion of the transitional metal increases the overlapping of orbitals of an impurity cation with those of four F ions, thereby increasing the covalence and lowering the impurity charge, and thus reduces the Madelung energy and the ground state relative to the conduction band.

Ni^+ Centers

Nickel impurities are incorporated into AEF crystals in the divalent state, isomorphically displacing the ions of the alkaline-earth metal. In CdF_2 , CaF_2 , and BaF_2 crystals activated by Ni, the major band of visible spectrum in the region of 16000–20000 cm^{-1} of the absorption spectra of Ni^{2+} ions is composed of three (or four) weakly resolved components, and the long-wavelength component caused by a spin-allowed transition is the one most intense (Fig. 2).

The X-ray coloring of $\text{CaF}_2\text{-Ni}^{2+}$ and $\text{SrF}_2\text{-Ni}^{2+}$ crystals results in the formation of monovalent Ni^+ ions that occupy off-center positions shifting in direction $\langle 100 \rangle$ to one of the edges, which is absolutely clear from the EPR data. The symmetry of centers is reduced to tetragonal C_{4v} . There are also centers with weakly perturbed tetragonal symmetry (orthogonal distortion) [9–13].

Wide intense bands in the absorption spectra are registered in the UV range of 200–400 nm after X-ray coloring at room temperature. If variations are observed in the absorption of Ni^{2+} centers, they are minor, testifying to the substantial difference between oscillator forces for the transitions of Ni^{2+} and Ni^+ centers (Fig. 2).

The absorption of Ni^+ centers is thus related to the allowed dipole transitions. Two cases are possible:

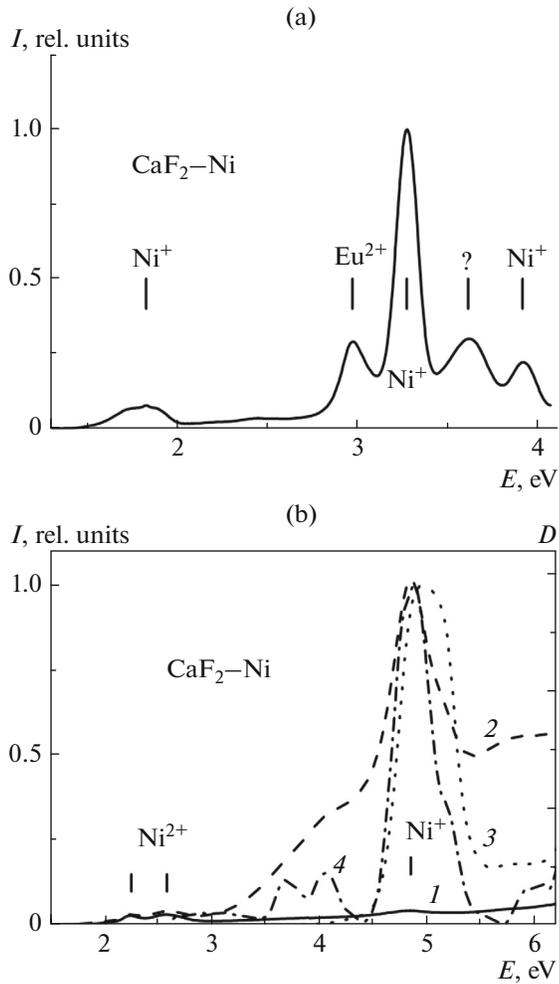


Fig. 2. (a) Luminescence spectrum of $\text{CaF}_2\text{-Ni}$ crystals at 77 K. (b) Absorption spectra at 300 K prior to (1) and after (2) X-ray irradiation at 300 K, excitation spectrum of 3.91 and 3.27 eV (3), and spectrum of luminescence excitation of 1.83 eV (4). D is the optical density

(i) charge transfer transitions from the valence band (allowed $p \rightarrow 3d$ transitions) and (ii) intracenter $3d \rightarrow 4p$ transitions. In [14], the absorption of Ni^+ centers was associated with intracenter $3d \rightarrow 4p$ transitions, but the authors ignored the results from a photoluminescence study of these centers.

When the Ni^+ centers in absorption bands are excited, two groups of luminescence bands are observed that are probably associated with two types of Ni^+ centers: high-energy, composed of two bands (317 and 379 nm), and low-energy in the red area of the spectrum. These spectra are very similar to those studied in [11, 15]. Our luminescence spectra can be explained using the scheme in Fig. 3. Absorption is associated with charge transfer transitions from the valence bands on Ni^+ ions, accompanied by the formation of $\text{Ni}^0 + \text{holes}$ complexes. The high-energy

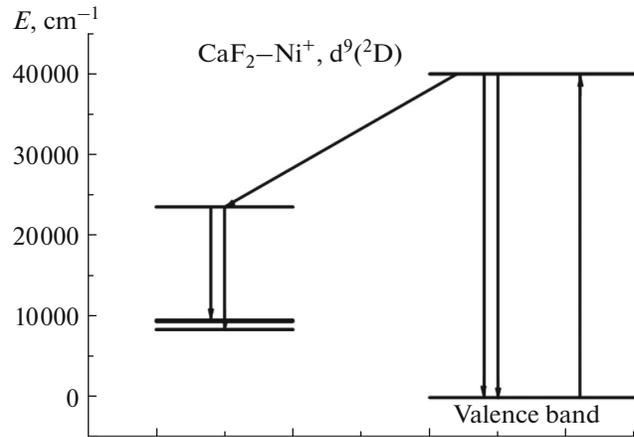


Fig. 3. Schematic position of Ni^+ levels in alkaline-earth fluorides.

luminescence bands are associated with the direct recombination of electrons and holes, while the low-energy luminescence bands are associated with recombination, upon which Ni^+ centers are formed in excited state. Intracenter luminescence of the Ni^+ centers is observed in this case as well. Possible transitions in the luminescence and absorption spectra upon charge transfer transitions were analyzed in [16].

Co^+ Centers

Cobalt impurities are inserted into AEF crystals in the divalent state, isomorphically displacing ions of the alkaline-earth metal. In Co-activated CdF_2 , CaF_2 , and BaF_2 crystals, the major band of visible spectrum in the region of 16000–20000 cm^{-1} is composed of three (or four) weakly resolved components, and the long-wavelength component caused by the ${}^4\text{F} \rightarrow {}^4\text{P}$ transition [17] is the one most intense.

Coloring of the AEFs (CaF_2 and SrF_2) activated by Co ions results in the formation of wide intense absorption bands in the region of 200–300 nm associated with the formation of Co^+ centers [18]. In $\text{CaF}_2\text{-Co}^{2+}$ crystals, the absorption bands that form during X-ray coloring are similar to those described in [19]. The formation of these bands is accompanied by slight (or in many cases unregistered) reductions in the absorption of Co^{2+} centers in the area of 16000–20000 cm^{-1} . This indicates that these centers are characterized by greater oscillator forces in absorption than were expected for transitions inside the d -envelope, so this absorption is probably associated with charge transfer transitions [16].

The photoexcitation of these absorption bands leads to luminescence, spectra of which are shown in Fig. 4 along with the excitation spectra of SrF_2 crystals. CaF_2 crystals exhibit similar spectra in which all

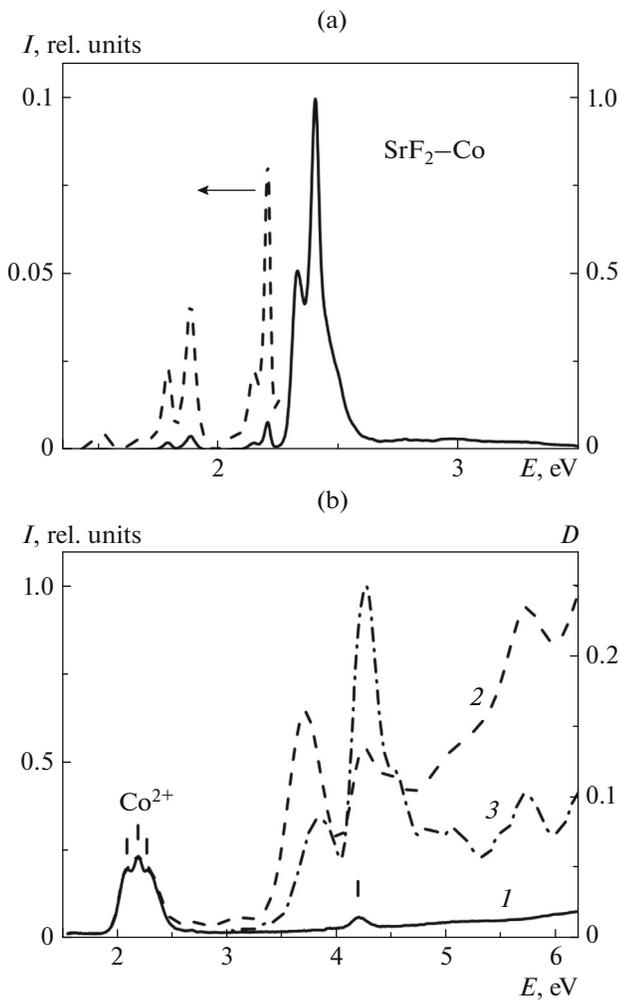


Fig. 4. (a) Spectra of luminescence at 77 K of $\text{SrF}_2\text{-Co}$ crystals. The second curve represents low-intensity luminescence multiplied by a factor of 10. (b) Absorption spectra at 300 K prior to (1) and after (2) X-ray irradiation at 300 K and excitation spectrum (3). D is the optical density.

bands in the luminescence spectrum are slightly shifted toward high energy. In many cases, d^8 ions (Co^+ , Ni^{2+}) luminesce in octahedral rather than tetrahedral positions, though there are apparently exceptions to this: it has been reported that ZnS:Ni^{2+} (sphalerite) crystals luminescence in tetrahedral positions [20].

Basically similar luminescence spectra (with worse resolution and in a lower energy range) have been registered for CaF_2 [21] and SrF_2 [18] crystals. In CaF_2 crystals, the absorption spectra were similar to those in [19], but we failed to reproduce the experimental data on Co^{++}F centers from this work: all bands were probably associated only with the absorption of Co^+ centers, which were also registered in the excitation and luminescence spectra.

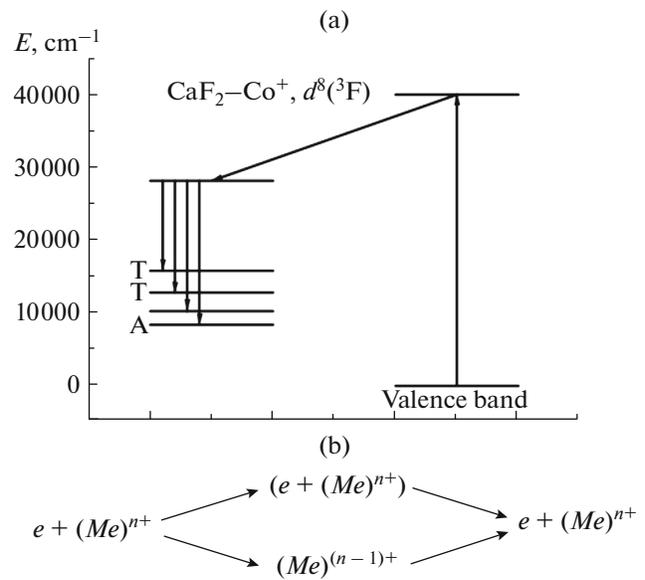


Fig. 5. (a) Schematic positions of Co^+ levels in alkaline-earth fluorides and (b) the approach of electron to an impurity divalent ion with and without the formation of a quasi-related state.

The luminescence spectra of both crystals were similar to $d-d$ transitions in Co^+ centers with $3d^8(^3F_4)$ configuration. In octahedral or cubic crystalline field 3F_4 , the state of d^8 ions is split into three levels: 3A_2 , 3T_1 , and 3T_2 . In an octahedral environment, state 3A_2 is characterized by the lowest energy; in contrast, it is characterized by the highest energy in a cubic environment.

Assuming that the most intense luminescence is observed upon the transition to the 3A_2 -level, and since it has the strongest energy when compared to other bands, we suggest that the 3A_2 state has the lowest energy (Fig. 5a). This indicates that Co^+ occupies positions other than cubic. Since, as was shown above, Co^+ is unstable in a cubic environment because its ground state lies in the conduction band, and (in analogy with Ni^+ centers) we may assume that Co^+ centers also occupy off-center positions with symmetry C_{4v} , in this case too state 3A_2 has the lowest energy. The positions of the levels are shown in Fig. 5a. A rough estimate of crystalline splitting yields values $D_q = 410$ and 390 cm^{-1} for CaF_2 and SrF_2 , respectively, which seems likely when compared to the similar values for the Co^{2+} and Ni^{2+} centers of these crystals [17].

Discussion

Below, we consider the processes that occur upon localization of the ground degenerate d -state on the conduction band (the formation of resonance states)

and which eventually lead to either the formation of anion vacancies near impurity ions or their off-center shifts due to an intensified Jahn–Teller effect. The irradiation of AEF crystals activated by divalent ions of transitional metals (Co^{2+} , Ni^{2+}) creates electrons in the conduction band that can be captured by impurities, forming short-lived quasirelated states of monovalent ions whose ground state is localized in the conduction band, as was shown by a rough estimate. They are referred to as resonance or autoionization states, since they can spontaneously decay on electrons and ions in the ground or excited states. An electron can also approach an impurity divalent ion without the formation of a quasi-related state. These two possibilities are described schematically in Fig. 5b.

The interference of these close states leads to the Feshbach resonances considered upon elastic and nonelastic neutron scattering through the formation of a compound nucleus in [22–24]. This concept was later extended to other branches of physics related to the resonance state. Three areas of physics now use Feshbach resonances:

(1) nuclear physics, for neutron scattering through the formation of a compound nucleus;

(2) the scattering of electrons (or other particles) on molecules and atoms (especially with the formation of negative ions);

(3) the scattering of free charge carriers in metals and semiconductors on impurities with electron states in the conduction band (although the resonance scattering of charge carriers in these materials is not limited by Feshbach resonances only).

The last two examples are the ones most similar to our processes. The main types of resonance states upon the scattering of electrons on molecules and atoms were described by Bardsley and Mandl [25]:

- (i) nuclear-excited Feshbach resonances;
- (ii) electron-excited Feshbach resonances;
- (iii) resonance forms.

Nuclear-excited Feshbach resonances are especially typical of molecules characterized by positive electron affinity. Electrons with energies close to zero are in this case captured on the nuclear-excited levels of ions. The electrons' kinetic energy is directly transferred to the movement of nuclei, so nuclear-excited resonance leads to violation of the Born–Oppenheimer approximation. In other words, nuclear-excited Feshbach resonances intensify the Jahn–Teller effect when electrons are captured in the degenerate ground d -state localized in the conduction band.

In many cases, the period of electron capture and autoionization is much shorter than the one associated with lattice distortion (the Jahn–Teller effect), so autoionization should lead to repeated electron capture and autoionization (valence fluctuation). In this

regard, valence fluctuations of an impurity ion are probably necessary for its off-center shift or the formation of an anion vacancy near it. On the other hand, nuclear-excited Feshbach resonances are characterized by longer lives than other processes of the resonance scattering of electrons on impurity ions, and this period is long enough for the distortion of the lattice around an impurity. Similar processes of dissociation decay occur when electrons are captured by molecules [26].

CONCLUSIONS

Rough estimates of the ground state of monovalent ions of transitional metals in alkaline-earth fluorides show that it is localized in the conduction band. The example of monovalent Co and Ni ions in CaF_2 and SrF_2 crystals shows that this scenario results in the unstable state of these ions in cubic environments.

A stable state is achieved by these ions shifting to off-center positions. It is assumed this shift is due to the formation of a resonance state upon electron capture by divalent ions, the decay of which due to the Jahn–Teller effect results in a considerable off-center shift of monovalent ions.

ACKNOWLEDGMENTS

This work was performed on equipment at the Shared Resource Center for Isotopic–Geochemical Research, Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences. It was supported by the Russian Foundation for Basic Research, project nos. 15-02-06666-a and 15-02-06514-a.

REFERENCES

1. Egranov, A.V. and Sizova, T.Yu., *Izv. Vyssh. Uchebn. Zaved., Fiz.*, 2013, vol. 56, no. 2-2, p. 134.
2. Egranov, A.V., Sizova, T.Yu., Shendrik, R.Yu., and Smirnova, N.A., *Bull. Russ. Acad. Sci.: Phys.*, 2015, vol. 79, p. 280.
3. Egranov, A.V. and Sizova, T.Yu., *J. Phys. Chem. Solids*, 2013, vol. 74, p. 530.
4. Egranov, A.V., Sizova, T.Yu., Shendrik, R.Yu., and Smirnova, N.A., *J. Phys. Chem. Solids*, 2016, vol. 90, p. 7.
5. Aramburu, J.A., Fernandez, P.G., Barriuso, M.T., and Moreno, M., *Phys. Rev. B*, 2003, vol. 67, p. 020101.
6. Garcia-Fernandez, P., Trueba, A., Garcia-Lastra, J.M., et al., *The Jahn-Teller Effect Fundamentals and Implications for Physics and Chemistry*, Köppel, H., Yarkony, D.R., and Barentzen, H., Eds., Springer, 2009, p. 415.
7. McClure, D.S., *Defects in Solids*, Hannay, N., Ed., Springer, 1975, p. 1.
8. McClure, D.S., *J. Lumin.*, 1979, vols. 18/19, p. 135.
9. Casas, J., den Hartog, H.W., and Alcalá, R., *J. Phys. Colloq.*, 1980, vol. 41, no. C6, p. 191.

10. Casas-Gonzalez, J., den Hartog, H.W., and Alcalá, R., *Phys. Rev. B*, 1980, vol. 21, p. 3826.
11. Alonso, P.J., Casas-Gonzalez, J., den Hartog, H.W., and Alcalá, R., *J. Phys. C*, 1983, vol. 16, p. 3593.
12. Alonso, P.J., Casas-Gonzalez, J., Alcalá, R., and den Hartog, H.W., *Radiat. Eff.*, 1983, vol. 73, p. 215.
13. Alonso, P.J., Casas-Gonzalez, J., den Hartog, H.W., and Alcalá, R., *Phys. Rev. B*, 1983, vol. 27, p. 2722.
14. Moreno, M., Aramburu, J.A., and Barriuso, M.T., *J. Phys. C*, 1986, vol. 19, p. L315.
15. Casas-Gonzalez, J., Alonso, P.J., den Hartog, H.W., and Alcalá, R., *J. Lumin.*, 1981, vol. 22, p. 139.
16. Dorenbos, P., *J. Phys.: Condens. Matter*, 2003, vol. 15, p. 8417.
17. Stolov, A.L. and Yakovleva, Zh.S., *Fiz. Tverd. Tela*, 1968, vol. 10, p. 1513.
18. Orera, J.M., Alcalá, R., and Alonso, P.J., *J. Phys. D*, 1981, vol. 14, p. 1923.
19. Alcalá, R. and Alonso, P.J., *Phys. Rev. B*, 1978, vol. 18, p. 5506.
20. Roussos, G. and Schulz, H.J., *Phys. Status Solidi (b)*, 1980, vol. 100, p. 577.
21. Alcalá, R. and Alonso, P.J., *J. Lumin.*, 1979, vol. 20, p. 1.
22. Feshbach, H., *Ann. Phys.*, 1958, vol. 5, p. 357.
23. Feshbach, H., *Ann. Phys.*, 1962, vol. 19, p. 287.
24. Feshbach, H., *Rev. Mod. Phys.*, 1964, vol. 36, p. 1076.
25. Bardsley, J.N. and Mandl, F., *Rep. Prog. Phys.*, 1968, vol. 31, p. 471.
26. Vorob'ev, A.S., Pshenichnyuk, S.A., Asfandiarov, N.L., and Nafikova, E.P., *Tech. Phys.*, 2014, vol. 59, p. 1277.

Translated by I. Yu. Melekestseva