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INVESTIGATION OF EPR PARAMETERS AND THE LOCAL STRUCTURE OF THE RHOMBIC Cu^{2+} CENTER IN ZINC FLUORIDE

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Based on a cluster approach, the local structure of the rhombic Cu^{2+} center in a ZnF_2 crystal is investigated by using the high-order perturbation formulas of electron paramagnetic resonance (EPR) parameters g-factors g_i ($i = x, y, z$) and hyperfine structure constants A_i in rhombically compressed octahedral symmetry. According to the studies, the local axial distortion angle $\Delta\alpha'$ ($\approx 2.9°$) in the impurity center is found to be by ~2.5° larger than the host value, which is characterized as a contraction and stretching of the parallel and perpendicular bond lengths by about 0.116 Å and 0.058 Å respectively. This results in a more compressed ligand octahedron because of the Jahn—Teller effect via the interaction of the vibrations of impurity-ligand bonds in the Cu^{2+} center. The reasonableness of the results is also discussed.

Keywords: electron paramagnetic resonance, defect structure, Cu^{2+}, ZnF_2.
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INTRODUCTION

ZnF_2 belongs to the rutile-type structure and is an important birefringent crystal with high optical transmittance from the vacuum ultraviolet to the infrared region of the spectrum [1]. ZnF_2 is also a useful material with interesting laser properties [2, 3], negative thermal expansion [4] and it is also an important component of glass materials [5—7]. The optical properties and unique luminescence and optical absorption behavior were especially extensively investigated for ZnF_2 doped with some transition metal (*e.g.*, Fe^{2+}, Mn^{2+}, and Ni^{2+}) ions [8—12]. In general, the above properties or behavior are sensitive to the local structure and electronic states of doped transition-metal impurities, which can be analyzed by means of the EPR technique. Among the transition-metal ions, Cu^{2+} can be regarded as a model system with a single $3d$ hole (corresponding to the only one ground state and one excited state under an ideal octahedron), which may exhibit unique EPR behavior. For example, the EPR experiments were performed for Cu^{2+} doped ZnF_2, and the EPR parameters (*i.e.*, the anisotropic g-factors g_i ($i = x, y, z$) and the hyperfine structure constants) were also measured [13]. Unfortunately, up to now, no satisfactory interpretation of the above experimental results has been made, and information about the local structure of the Cu^{2+} center in ZnF_2 has not been obtained yet. To explain these EPR results, the simple perturbation formulas of the EPR parameters for a $3d^9$ ion in rhombically compressed octahedra were adopted by the author. Nevertheless, the contributions from the low symmetrical distortion (or the local structure) were simply considered by introducing various adjustable parameters, instead of a quantitative calculation from a uniform theoretical model. So, the previous treatments (see [13]) failed to connect the EPR spectra with the local structures of the impurity center.

Since (i) the information about the local structure of Cu^{2+} in ZnF_2 would be useful to understand the impurity properties and behavior in this material and (ii) the studies of EPR parameters for Cu^{2+} in

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compressed octahedra are relatively less than those in the elongated octahedron, theoretical investigations of these EPR parameters and the local structure in this system are of fundamental and practical significance. In this work, the high (fourth) order perturbation formulas for a $3d^9$ ion under rhombically compressed octahedra are used to analyze the above EPR parameters for the impurity Cu^{2+} centers by considering the reasonable local axial distortion angle $\Delta\alpha'$ in a $[CuF_6]^{4-}$ cluster of $ZnF_2:Cu^{2+}$ due to the Jahn—Teller effect (JTE).

CALCULATIONS

The studied ZnF_2 crystal has the same rutile structure and belongs to the D_{2h} space group symmetry [13]. It contains divalent metal Zn^{2+} ions, each of which is surrounded by six fluoride ligands forming a distorted slightly compressed octahedron with the distances $R_{\|} \approx 2.015$ Å and $R_{\perp} \approx 2.043$ Å from the nearest six fluoride ions and the planar bonding angle $\theta \approx 79.8°$ [13]. The above low symmetrical distortions in the host Zn^{2+} site can be mainly characterized by the axial distortion angle $\Delta\alpha = \alpha - \alpha_0$ with $\alpha \approx \tan^{-1}(R_{\perp}/R_{\|})$ and $\alpha_0 \approx 45°$ of the cubic symmetry. Thus, we have $\Delta\alpha \approx 0.4°$ [13]. Additionally, the ligand octahedron for this site also suffers a perpendicular (or rhombic) distortion ($\theta < \theta_0 = 90°$ of the cubic case).

For a $3d^9(Cu^{2+})$ ion in rhombically compressed octahedra, its lower orbital doublet ${}^2E_g$ would be separated into two singlets ${}^2A_{1g}(\theta)$ and ${}^2A'_{1g}(\varepsilon)$, with the former lying lowest. Meanwhile, the higher orbital triplet ${}^2T_{2g}$ of the cubic case would be split into three singlets: ${}^2B_{1g}(\zeta)$, ${}^2B_{2g}(\eta)$ and ${}^2B_{3g}(\xi)$ [14]. As mentioned before, the simple perturbation formulas of these EPR parameters were adopted [13] by neglecting the local axial distortion instead of various adjustable parameters (molecular orbital coefficients a, b, c, d, ξ, the dipolar hyperfine structure parameter P, and the core polarization constant κ) that may not well treat this impurity center. In order to investigate more exactly these EPR parameters for the impurity Cu^{2+} center in ZnF_2, some improvements can be performed by including the contributions from the lower symmetry (*e.g.*, rhombic) distortion. In addition, for the studied Cu^{2+} center in ZnF_2 with a $[CuF_6]^{4-}$ cluster, the covalency of the studied system can be insignificant, and the ligand spin-orbit coupling coefficient is much smaller than that of the central ion. So, the conventional crystal-field model can be conveniently adopted here. Thus, the perturbation formulas of the EPR parameters for the rhombically compressed octahedra of the $3d^9$ cluster can be written as follows:

$$\begin{aligned}
g_x &= g_s + 6k\varsigma / E_3 + 3k\varsigma^2 / (E_3E_4) + (3/4)g_s\varsigma^2(1/E_3^2 - 1/E_4^2) + \\
&\quad + [(3/4)g_s\varsigma^3 / (E_3E_4)(1/E_4 - 1/E_3)] - [3k\varsigma^3 / E_3]\{1/(E_3E_4) + \\
&\quad + 1/(E_2E_3) - 1/(E_2E_4)\} - (3/2)\varsigma^2(1/E_4 - 1/E_3)(k\varsigma/(E_1E_3) + k\varsigma/(E_2E_4)), \\
g_y &= g_s + 6k\varsigma / E_4 + 3k\varsigma^2 / (E_3E_4) + (3/4)g_s\varsigma^2(1/E_4^2 - 1/E_3^2) + \\
&\quad + [(3/4)g_s\varsigma^3 / (E_3E_4)(1/E_3 - 1/E_4)] - [3k\varsigma^3 / E_4]\{1/(E_3E_4) + \\
&\quad + 1/(E_2E_4) - 1/(E_2E_3)\} - (3/2)\varsigma^2(1/E_3 - 1/E_4)(k\varsigma/(E_1E_4) + k\varsigma/(E_2E_3)), \\
g_z &= g_s - 3k\varsigma^2 / (E_3E_4) + (3/4)g_s\varsigma^2(1/E_3^2 + 1/E_4^2) + \\
&\quad + [(3/2)k\varsigma^3 / (E_3E_4)](1/E_3 + 1/E_4) + [(3/2)g_s\varsigma^3 / (E_3E_4)(1/E_3 + 1/E_4)], \\
A_x &= P_0[-(\kappa + \kappa') - 2H/7 + 15(g_x - g_s)/14], \\
A_y &= P_0[-(\kappa - \kappa') - 2H/7 + 15(g_y - g_s)/14], \\
A_z &= P_0[-\kappa + 4H/7 + (g_z - g_s) - (g_x + g_y - 2g_s)/14]. \qquad (1)
\end{aligned}$$

Here g_s (≈ 2.0023) is the spin-only value, k is the orbital reduction factor, characteristic of the covalency effect of the studied systems, ζ is the spin-orbit coupling coefficient, and P_0 is the dipolar hyperfine structure parameter for the free Cu^{2+}ion ($3d^9$) in crystals. Factors κ and κ' are, respectively, the core polarization constant of the isotropic and anisotropic parts, similar to the treatment in the previous work [15]. H is the reduction factor due to the central ion $3d$—$3s$ (—$4s$) orbital admixtures arising from the low symmetrical (rhombic) distortion, which brings forward some anisotropic contributions to the hyperfine structure constants. The denominators E_i ($i = 1$—4) denote, respectively, the energy separations between the excited $^2A'_{1g}(\varepsilon)$, $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$, and $^2B_{3g}(\xi)$ and the ground $^2A_{1g}(\theta)$ states. They can be determined from the energy matrices of a $3d^9$ ion under rhombic symmetry in terms of the cubic field parameter D_q and the rhombic field parameters D_s, D_t, D_ξ, and D_η

$$\begin{aligned}
E_1 &= 4D_s + 5D_t,\\
E_2 &= 10D_q + 4D_s + 5D_t,\\
E_3 &= 10D_q + D_s + 10D_t - 3D_\xi + 4D_\eta,\\
E_3 &= 10D_q + D_s + 10D_t + 3D_\xi - 4D_\eta.
\end{aligned} \tag{2}$$

The rhombic field parameters can be expressed from the local geometry and the superposition model as follows [16]:

$$\begin{aligned}
D_s &= -(4/7)\bar{A}_2(R_0)[(R_0/R'_\perp)^{t_2} - (R_0/R'_\parallel)^{t_2}],\\
D_t &= (4/21)\bar{A}_4(R_0)[(7\cos 2\theta + 3)(R_0/R'_\perp)^{t_4} - 4(R_0/R'_\parallel)^{t_4}],\\
D_\xi &= (4/7)\bar{A}_2(R_0)(R_0/R'_\perp)^{t_2}\cos\theta,\\
D_\eta &= (20/21)\bar{A}_4(R_0)(R_0/R'_\perp)^{t_4}\cos\theta,
\end{aligned} \tag{3}$$

where $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents in view of the ionic nature of the bonds [16, 17]. $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ are the intrinsic parameters, with the reference bond length R_0 taken as the average metal-ligand distance, *i.e.* $R_0 = \bar{R} = (R_\parallel + 2R_\perp)/3 \approx 2.034$ Å [13]. For $3d^n$ ions under octahedral crystal-fields, the relationships $\bar{A}_4(R_0) \approx (3/4)D_q$ [18] and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range 8 ~ 12 obtained for $3d^n$ clusters in many crystals [18—20], thus, we take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. As mentioned before, when the impurity Cu^{2+} substitutes for the host Zn^{2+} site, the Jahn—Teller Cu^{2+} ion can suffer JTE under the octahedral environment by a contraction or stretching of the parallel and perpendicular bond lengths. Consequently, the impurity-ligand bond lengths $R'_\parallel$ and $R'_\perp$ and hence the angle $\alpha' \approx \tan^{-1}(R'_\perp/R'_\parallel)$ may be different from those ($R_\parallel$, $R_\perp$ and α) in the host. Thus, the impurity-ligand bond lengths can be written in terms of the local distortion angle $\Delta\alpha'$ ($= \alpha' - \alpha_0$) and the average distance $\bar{R}$ as

$$R'_\parallel \approx \frac{3\bar{R}}{1 + 2\tan(45^0 + \Delta\alpha')}, \qquad R'_\perp \approx \frac{3\bar{R}}{2 + \cot(45^0 + \Delta\alpha')}. \tag{4}$$

For $ZnF_2:Cu^{2+}$, to our knowledge, the spectral parameters D_q and k were not reported. However, they can be acquired from those ($D_q \approx 696$ cm^{-1} and $k \approx 0.92$ [17]) for the similar compressed octahedra of the $[CuF_6]^{4-}$ cluster in $Ba_2ZnF_6:Cu^{2+}$ (with $R_0 \approx 2.05$ Å) [17]. According to the relationship $D_q \propto R^{-5}$ [21, 22], the spectral parameters $D_q \approx 671$ cm^{-1} and $k \approx 0.92$ can approximately adopted for the EPR parameters of $ZnF_2:Cu^{2+}$ investigated here. Then the spin-orbit coupling coefficient ζ for Cu^{2+} in the ZnF_2 crystal can be written as the free-ion value ζ_0 (≈ 829 cm^{-1} [18]) multiplying k. Substituting these values (and also the host structural parameters of Zn^{2+} sites in ZnF_2) into equation (1), the g factors are calculated (Cal.^{a}) and shown in Table 1. It can be found that the theoretical EPR parameters (Cal.^{a}) based on the host structural parameters (*i.e.*, the host axial distortion angle $\Delta\alpha$) do not agree well with the experimental data. This means that the host axial distortion angle $\Delta\alpha$ is unsuitable for the EPR analysis of the impurity centers. In fact, the immediate environments around the impurity Cu^{2+} are usually dissimilar to those of the host Zn^{2+} site in ZnF_2 due to the JTE via the interaction of the vibrations of impurity-ligand bonds in the impurity Cu^{2+} center. Similar modifications in the local structures were also reported for the V^{4+} ion in the interstitial site of a TiO_2 crystal [15]. Therefore,

Table 1

The g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) *for the rhombic* Cu^{2+} *center in* ZnF_2

	g_x	g_y	g_z	A_x (^{63}Cu)	A_y (^{63}Cu)	A_z (^{63}Cu)
Cal.[a]	2.642	2.482	2.013	71.6	44.4	43.3
Cal.[b]	2.426	2.356	2.006	–18.5	–8.0	50.1
Expt. [13]	2.4275	2.354	2.061	18.3	7.7	49.9

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[a] Calculations based on the high order perturbation formulas in equation (1) and the host structural parameters (*i.e.*, $\Delta\alpha' \approx 0.4°$).

[b] Calculations based on the high order perturbation formulas in equation (1) and the local structural parameters (*i.e.*, $\Delta\alpha' \approx 2.9°$).

the host planar bond lengths $R_{\parallel}$ and $R_{\perp}$ in equation (3) should be replaced by the local $R'_{\parallel}$ and $R'_{\perp}$ due to JTE via the interaction of the bond vibrations. Substituting the related values into equation (1) and fitting the calculated *g* factor to the experimental data, we have

$$\Delta\alpha' \approx 2.9°. \tag{5}$$

In the formulas of the hyperfine structure constants, the dipolar hyperfine structure parameter P_0 is 388×10^{-4} cm^{-1} for the free ^{63}Cu ion [18]. The isotropic core polarization constant can be determined from the relationship $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$, where χ is characteristic of the density of unpaired spins at the nucleus of the central ion and $\langle r^{-3}\rangle$ is the expectation value of the inverse cube of the 3*d* radial wave function. From the data $\langle r^{-3}\rangle \approx 8.252$ a.u. [14] and $\chi \approx -3.0$ a.u. [23] for Cu^{2+} in some oxides and nitrides crystals and can be approximately applied. Thus, the value $\kappa \approx 0.24$ may be estimated and used for the studied system here. This result very close to that the previous κ (≈ 0.26 [13]) and can be regarded as reasonable. The reduction factor *H* is taken as 0.736 in view of the Cu^{2+} 3*d*—3*s* (—4*s*) admixtures due to the rhombic distortion, about 26 % smaller than the ideal value of unit in the absence of the low symmetrical distortion. Interestingly, this value is actually very close to that (≈ 0.78 [24]) for the rhombic elongated octahedral Cu^{2+} center in TiO_2. Nevertheless, for the studied ZnF_2:Cu^{2+} here, owing to larger compression for the $[CuF_6]^{4-}$ cluster and thus lead to higher Cu^{2+} 3*d*—3*s* (—4*s*) orbital admixtures. Hence, the adopted *H* (≈ 0.736) for ZnF_2:Cu^{2+} is comparable with but smaller than that *H* (≈ 0.78 [24]) for the studied TiO_2:Cu^{2+} based on the EPR analyzed can be understand.

Substituting the above parameters into equation (1) and fitting the calculated hyperfine structure constants A_i ($i = x, y, z$) to the observed values, the anisotropic core polarization constant can be obtained

$$\kappa' \approx 0.051. \tag{6}$$

The corresponding EPR parameters (Cal.[b]) are shown in Table 1. For comparison, the theoretical results (Cal.[a]) based on the host axial distortion angle $\Delta\alpha$ in pure crystals are also shown in Table 1.

DISCUSSION

Table 1 reveals that the EPR parameters (Cal.[b]) for the Cu^{2+} center in ZnF_2 calculated based on the local axial distortion angle $\Delta\alpha'$ ($\approx 2.9°$) show better agreement with the observed values than those (Cal.[a]) based on host $\Delta\alpha$ in the pure crystal. Thus, the EPR spectra for Cu^{2+} in the rutile-type ZnF_2 crystal are uniformly interpreted, and the information about the local structure of the impurity center is obtained, too.

(1) The local axial distortion angle $\Delta\alpha'$ ($\approx 2.9°$) obtained here is by about 2.5° larger than that ($\Delta\alpha \approx 0.4°$) in the host, which may be characterized as a contraction and stretching of the parallel and perpendicular bond lengths by about 0.116 and 0.058 Å respectively, due to the JTE via the interaction

of the vibrations of the parallel and perpendicular impurity-ligand bonds. As a result, the ligand octahedron is more compressed than the host. In fact, the axial distortion parameters (D_s and D_t) based on the host angle $\Delta\alpha$ would be underestimated and then result in larger g_x and g_y (Cal.^{a} in Table 1). Thus, the local angle $\Delta\alpha'$ accounting for the larger axial distortion leads to lower and better theoretical g_x and g_y (Cal.^{b} in Table 1). In addition, the effective planar bonding angle (labeled as θ') around Cu^{2+} may also be different from θ in the host because of the occupation of the impurity. In fact, the contributions from the low symmetrical crystal fields are mainly axial (D_s and D_t) because of the large distortion angle $\Delta\alpha'$ (equation (3)). On the contrary, the contributions from the perpendicular (rhombic) ones (D_ξ and D_η) are relatively less important. Thus, for the sake of reduction in the number of adjustable parameters, the variation of the planar bonding angle is not considered here for simplicity. Of course, the determination of the local structures for transition-metal ions in compounds is actually a difficult problem, involving various complicated physical and chemical properties of the impurities and the hosts. In addition, the JTE produces not only the static distortions of the impurity center, but it also affects the dynamics of the impurity, which can be seen in the angular dependence of EPR spectrum [25]. Therefore, the information about the local structures (*i.e.*, the local axial distortion angle $\Delta\alpha'$ ($\approx 2.9°$)) for $ZnF_2:Cu^{2+}$ obtained in this work should be regarded as tentative one, which remains to be further verified with experimental measurements.

(2) The studied system has weak covalency (described as the covalency factor $N \approx 0.92 \approx 1$) due to the dominant ionicity of the Cu—F combination. In addition, the spin-orbit coupling coefficient (≈ 220 cm^{-1} [26]) of the fluoride is much smaller than that (≈ 829 cm^{-1} [18]) of the central Cu^{2+} ion. Thus, the perturbation formulas of the EPR parameters based on the conventional crystal-field model are the suitable approximations, and the ligand orbital and spin-orbit coupling contributions may be ignored for simplicity. In addition, the orbital reduction factor (or covalency factor) is usually determined from the relationship $k \approx \varepsilon = 1 - h(L)k(M)$, where ε is the square of the covalency factor, and $h(L)$ and $k(M)$ are the characteristics of the ligand and central metal ions respectively. For Cu^{2+} in fluoride octahedra, $k(M) \approx 0.3$ [27] as well as $h(L) \approx 0.9$ [27] yield $k \approx 0.88$. This value is very close to k (≈ 0.92) adopted for the studies of $ZnF_2:Cu^{2+}$, and can be regarded as reasonable.

(3) For the hyperfine structure constants, the results (A_x, A_y, and A_z in Cal.^{a}) calculated based on the host local axial distortion angle $\Delta\alpha$ are not as good as those (Cal.^{b}) based on the local ones. This means that JTE-induced local lattice distortions around Cu^{2+} have significant effects on the g factors (g_x and g_y), and hence, on the anisotropic parts of the hyperfine structure constants (equation (1)). Secondly, the optimal anisotropic core polarization constants κ' (≈ 0.051, which are much smaller than isotropic $\kappa \approx 0.24$) also attribute some anisotropic contributions to the A factors. Of course, the adoption of various adjustable parameters in the previous work [13] may also conceal the errors due to the omission of local lattice distortions. Consequently, the qualitative consistence between theory and experiment was accurately achieved for the A factors in the previous treatments [13]. However, in their calculations, the dipolar hyperfine structure parameter P ($\approx 164.5\times10^{-4}$ cm^{-1} [13]) for ^{63}Cu is much smaller than P_0 ($\approx 388\times10^{-4}$ cm^{-1} [18]) for the free ^{63}Cu ion, and the P/P_0 value (≈ 0.42) characterizes the strong covalency of the Cu^{2+}—F^- combination, which is inconsistent with that the Cu—F combination should have dominant ionicity (or insignificant covalency), as the experience and EPR investigation show for $Ba_2ZnF_6:Cu^{2+}$ with the same compressed $[CuF_6]^{4-}$ cluster ($k \approx 0.92$ [17] characterizes insignificant covalency). By the way, only the absolute values of the hyperfine structure constants were obtained in the experimental measurements. However, according to the calculations in the previous [13] and present works, the positive sign of A_z and the negative signs of A_x and A_y can be determined here.

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REFERENCES

1. *Belanger D.P., King A.R., Jaccarino V.* // Phys. Rev. B. – 1984. – **29**. – P. 2636 – 2643.
2. *Gastev S.V., Hoffman K.R., Kaveev A.K., Reeves R.J., Sokolov N.S.* // J. Cryst. Growth. – 2004. – **268**. – P. 536 – 542.
3. *Ko J.M., Tozawa S., Yoshikawa A., Inaba K., Shishido T., Oba T., Oyama Y., Kuwabara T., Fukuda T.* // J. Cryst. Growth. – 2001. – **222**. – P. 243 – 248.
4. *Chatterji T., Zbiri M., Hansen T.C.* // Appl. Phys. Lett. – 2011. – **98**. – P. 181911.
5. *Patil S.D., Jali V.M., Anavekar R.V.* // Bull. Mater. Sci. – 2009. – **32**. – P. 597 – 601.
6. *Gandhi Y., Venkatramaiah N., Kumar V.R., Veeraiah N.* // Physica B. – 2009. – **404**. – P. 1450 – 1464.
7. *Cheng L., Zheng L., Li G., Yuan K., Gu Y., Zhang F.* // J. Amer. Ceram. Soc. – 2010. – **93**. – P. 44 – 47.
8. *Wang S.J., Kuang X.Y., Duan M.L., Zhang C.X., Lu C.* // Phys. Status Solidi (b). – 2010. – **247**. – P. 416 – 421.
9. *Sugiura C.* // J. Phys. Soc. Jpn. – 1991. – **60**. – P. 2710 – 2717.
10. *Mukherji A., Das T.P.* // Phys. Rev. – 1958. – **111**. – P. 1479 – 1482.
11. *Feng W.L., Quan X.J., Hu N.* // Phil. Mag. Lett. – 2008. – **88**. – P. 287 – 291.
12. *Dürr U., Weber R.* // Phys. Status Solidi (b). – 1973. – **60**. – P. 733 – 738.
13. *Swalen J.D., Johnson B., Gladney H.M.* // J. Chem. Phys. – 1970. – **52**. – P. 4078 – 4086.
14. *Abragam A., Bleaney B.* Electron Paramagnetic Resonance of Transition Ions. Oxford University Press, London, 1970.
15. *Lin J.Z., Wu S.Y., Fu Q., Zhang H.M.* // Radiat. Eff. & Defects. – 2006. – **161**. – P. 571 – 577.
16. *Newman D.J., Ng B.* // Rep. Prog. Phys. – 1989. – **52**. – P. 699 – 763.
17. *Zhang D.T., He L., Yang W.Q., Zheng W.C.* // J. Lumin. – 2009. – **129**. – P. 1371 – 1374.
18. *Mei Y., Zheng W.C., He L.* // Spectrochim. Acta A. – 2009. – **72**. – P. 515 – 517.
19. *Newman D.J., Pryce D.C., Runciman W.A.* // Amer. Mineral. – 1978. – **63**. – P. 1278 – 1281.
20. *Zhang H.M., Wu S.Y., Lu G.D., Wei L.H., Zhang Z.H.* // J. Alloy. Compd. – 2008. – **464**. – P. 18 – 22.
21. *Moreno M.* // J. Phys. Chem. Solids. – 1990. – **51**. – P. 835 – 859.
22. *Moreno M., Barriuso M.T., Aramburu J.A.* // Int. J. Quantum Chem. – 1994. – **52**. – P. 829 – 835.
23. *McGarvey B.R.* // J. Phys. Chem. – 1967. – **71**. – P. 51 – 66.
24. *Zhang H.M., Wu S.Y., Xu P., Li L.L.* // Mod. Phys. Lett. B. – 2010. – **24**. – P. 2357 – 2364.
25. *Bersuker B.* The Jahn—Teller Effect. Cambridge University Press, New York, 2006.
26. *McPerson G.L., Kach R.C., Stucky G.D.* // J. Chem. Phys. – 1974. – **60**. – P. 1424 – 1431.
27. *Jørgensen C.K.* Absorption spectra, chemical bonding in complexes. Pergamon Press, Oxford, 1962.