



Theoretical study of the polarized electronic absorption spectra of vanadium-doped zircon

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Abstract

The polarized electronic absorption spectra of a blue vanadium-doped zircon single crystal, grown by the flux method, has been studied by quantum chemical (CI) calculations in order to determine the position of the V^{4+} dopant in the zircon host structure. Particularly, the excitation energies and polarizations of V^{4+} occupying alternate positions, either the zirconium or silicon position or the interstitial site $16g$, have been considered. It is concluded that the observed electronic absorption spectra and the color of zirconblue can only be explained if the V^{4+} chromophore is placed on the respective interstitial position.

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1. Introduction

Vanadium-doped zircon ($ZrSiO_4:V$) is an important industrial pigment [1, 2] because of its strong blue color combined with superior thermal and chemical stability of the zircon host matrix, which allows a variety of applications. The dopant V^{4+} has been shown to be the reason for the color of the pigment [3], but to date no conclusive proof has been obtained on the crystallographic site occupied by vanadium despite extensive research in this field.

In the main, the substitution of vanadium for zirconium and silicon, being the two most obvious possibilities, have been studied extensively. As both the zirconium and the silicon position (V_{Zr} and V_{Si}) have the same site symmetry D_{2d} , there is no differentiation concerning the spectroscopic selection rules, which leads to difficulties in unambiguously interpreting the observed spectroscopic data. Thus, Demiray et al. [3]

suggested, based on the absorption spectrum of vanadium-doped zircon powders, that V^{4+} ions are located at the distorted dodecahedral site of Zr^{4+} (eight-fold coordinated ions, site symmetry D_{2d}). While lattice-energy calculations [4] supported this hypothesis, other experiments rather suggested a substitution for Si^{4+} (distorted tetrahedral site, site symmetry D_{2d}). From the electronic absorption (EAS) and electron spin resonance (ESR) spectra of single crystals, Di Gregorio et al. [5] concluded that V^{4+} substituted for Si^{4+} . This suggestion appeared to be in good agreement with results obtained by Raman spectroscopy [6]. Yet an alternative interpretation of ESR and electronic data led to the conclusion that V^{4+} substituted for both zirconium and silicon [7, 8]. This latter alternative, too, was supported by lattice-energy calculations [9].

A third possibility to incorporate vanadium was recently discovered by X-ray crystallography [10]. It is the insertion into the interstitial, strongly distorted tetrahedrally coordinated site $16g$ of space group $I4_1/amd$ with site symmetry C_2 and $x=0.25$ (second setting) [10, 11]. The charge balance is maintained

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through silicon vacancies. This proposal appears insofar convincing as the V–O distances for V in the interstitial site are in close agreement with calculated bond lengths [10]. The aim of this work is to determine the site into which vanadium is doped in zirconblue and to find a satisfactory explanation for the polarized EAS of a single crystal. The three alternate sites for V^{4+} in the zircon lattice, namely the substitution for zirconium (V_{Zr}), for silicon (V_{Si}) and the insertion into the interstitial site (V_{int}) were investigated employing group theoretical and quantum chemical methods.

2. Experimental

Single crystals of vanadium-doped zircon were grown by the flux method using a mixture of activated oxides as starting material, prepared by co-precipitation of zirconiumpropylate (Fluka 96596) and tetraethylorthosilicate (Aldrich 20,527-3). The binary oxide $ZrSiO_4$ with $MoO_3/Li_2MoO_4/V_2O_5$ or $LiVO_3/V_2O_5$ as both, flux and dopant material, was filled into a platinum crucible with tightly fitting lid and heated at $1250^\circ C$ for 10 h. By applying a cooling rate of $10^\circ C/h$, dark blue crystals up to 4 mm long were obtained. The highest content of the dopant vanadium with an almost black appearance of the single crystals was achieved by heating a mixture of 1.5g $ZrSiO_4$, 5.5g $LiVO_3$ and 28g V_2O_5 . However, best results concerning both color and crystal quality of the single crystals were obtained with 1.09g $ZrSiO_4$, 27g MoO_3 , 5.4g Li_2MoO_4 and 6g V_2O_5 . The resulting large dark blue, strongly dichroic crystals form idiomorphic tetragonal elongated prisms with dipyrimal faces. They were identified by X-ray diffraction. Depending on the content of the dopant vanadium, slightly different lattice constants were found. The inhomogeneity of the blue color within some crystals point to zonation of the contents of the dopant vanadium. It is worth noting that the most intense color occurs always in the core, forming often sharp interfaces with the less strongly, undolously colored outer parts. The contents of vanadium, zirconium and silicon in the single crystals were determined by means of an electron microprobe analysis (Camebox Microbeam). The polarized electronic absorption spectra of a dark blue, oriented single crystal were measured at room temperature in the range $4000\text{--}36000\text{ cm}^{-1}$ by means of microscope-spectrometric methods [12, 13]. The crystal studied by polarized EAS was oriented by X-ray oscillation photographs, ground and polished from both sides to obtain a plane parallel platelet parallel to c with a thickness of $t = 149\ \mu m$ as determined from the optical retardation [14]. Nearly 100% linearly polarized measuring radiation in the entire spectral range was obtained in the instrument used by a Glan-Thompson-type calcite polarizer. The spectral slit and step width were 50 cm^{-1} . The diameter of the measuring

spot was $42\ \mu m$ and within a homogeneous dark blue part of the crystal. The spectral reference position of the I_0 -measurement was set into the quartz platelet parallel to c next to the zircon crystal (cf. [12]).

The absorption spectra were evaluated with group theoretical tools to study the effect of symmetry reduction on the splitting of the d -orbitals. By this, the number of electronically allowed transitions of V^{4+} and their polarizations for the two site symmetries under discussion, D_{2d} of V_{Zr} and V_{Si} or C_2 of V_{int} , were determined. These sites correspond to the crystallographic sites $4a$, $4b$ and $16g$ for zirconium, silicon and the interstitial site, respectively. In case of the interstitial tetrahedral site, it was taken into account that its C_2 -axis coincides with the $[110]$ direction of the tetragonal crystal.

Quantum chemical calculations were carried out in order to determine quantitatively the expected energies of the excited states of V^{4+} , their polarizations and the ordering of the d -energy levels for each possible site. In addition, the transition probabilities of the electronically allowed transitions were calculated. These calculations were carried out using the MOLCAS [15] and DIESEL-CI [16] program packages.

3. Experimental results and definitions

The polarized electronic absorption spectra of zirconblue are shown in Fig. 1. They reveal three absorption bands in the IR and visible region, which can be assigned to d - d -absorptions of V^{4+} . Their positions, polarizations and intensities are given in Table 1. The intensity of the absorption bands depends on the content of vanadium in the crystal. In the crystal analyzed here, approximately 0.76 at% of vanadium is incorporated into the structure of zircon as determined by microprobe analysis. The analysis of several

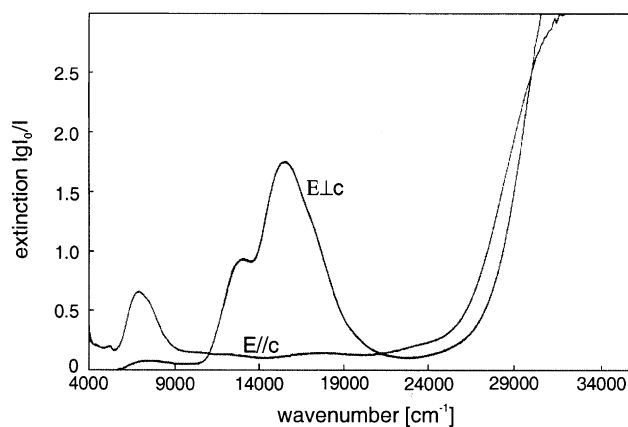


Fig. 1. Polarized electronic absorption spectra at 300 K of vanadium-doped zircon. The bands observed and assigned to d - d -transitions of V^{4+} are listed in Table 1.

Table 1

Properties of absorption bands originating from electronic transitions of V^{4+} in zircon, measured at room temperature, as obtained from the spectra of Fig. 1

Transition energy, observed (eV)	Polarization	Extinction coefficient $\lg I_0/I$	Assigned transitions
0.93	$E_{\parallel c}$	0.67	$A \rightarrow B$
1.61	$E_{\perp c}$	0.93	$A \rightarrow A$
1.94	$E_{\perp c}$	1.75	$A \rightarrow A$

vanadium-doped zircon crystals demonstrates that the silicon content decreases with increasing vanadium content, while the zirconium content is unaffected. This negative correlation of the silicon and vanadium contents indicates clearly that the substitution for zirconium, postulated by many authors, can be ruled out. Details of the microprobe analyses are given in [10].

4. Symmetry reduction

If a single d -electron is placed at the center of a tetrahedron or dodecahedron of ligands, its initial five-fold degeneracy is partially removed, resulting in an ${}^2E^c$ ground state and a 2T_2 excited raised above ${}^2E^c$. (The superscripts c and t are used to distinguish cubic E representations from tetragonal ones.) By further lowering the symmetry to D_{2d} , the degenerate cubic states are split. The irreducible representations of the resulting states are 2A_1 and 2B_1 , derived from the ${}^2E^c$ ground state, and 2B_2 and ${}^2E^t$, derived from 2T_2 . C_2 finally leads to the removal of all degeneracies. Whereas the irreducible representations of the resulting states can easily be derived ($3 \times {}^2A$, $2 \times {}^2B$ states), the determination of their sequence with rising energy is not possible by group theoretical or qualitative energetic considerations. For either case of symmetry reduction, D_{2d} or C_2 , the electronically allowed transitions and their polarizations are shown in Fig. 2, taking 2A_1 (D_{2d}) and 2A (C_2) as ground states, respectively.

The internal coordinate system for the site symmetry D_{2d} used here is based on a choice of axes which corresponds to the conventional setting in the cubic (T_d) symmetry (z parallel to c). For the interstitial site (site symmetry C_2), the only symmetry element present is oriented in the a,b -plane parallel to the [110] direction. In our group theoretical and quantum chemical treatment, the internal axes of the vanadium centered polyhedron are chosen as follows: x lies parallel to C_2 [110] and z perpendicular to C_2 , that is parallel to the crystal's main axis c [001]. This is useful for the symmetry reduction to be performed to reach C_2 and to compare the results of D_{2d} and C_2 . In order to distinguish the crystal coordinate system from the

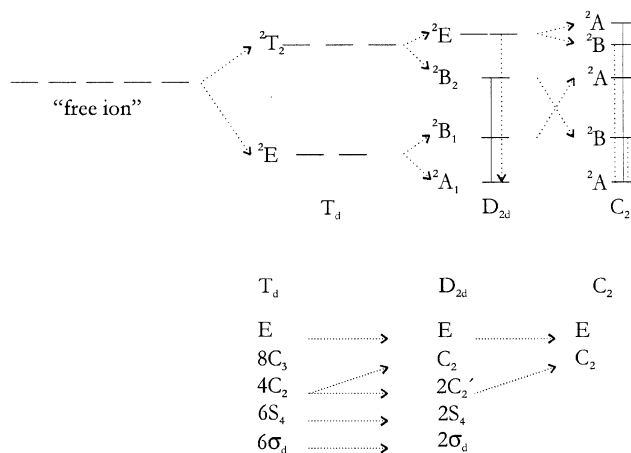


Fig. 2. Splitting of the 2D spectroscopic free-ion state of V^{4+} in crystal fields of decreasing symmetries from the tetrahedral (T_d), over the tetragonal (D_{2d}) to the monoclinic (C_2) coordination. Only electronically allowed transitions are shown. In D_{2d} , z -polarized transitions are shown by full lines, (x,y) -polarized by dashed lines. In C_2 , x -polarized transitions are shown by full lines, y - and z -polarized ones by dashed lines.

internal coordinate systems used, crystal coordinate axes are named a , b , c , and internal coordinate axes x , y , z .

5. Determination of allowed transitions by group theory

Group theoretical considerations show that in the point symmetry D_{2d} (V_{Zr} or V_{Si}) two energetically different $d-d$ -transitions of V^{4+} are electronically allowed if the ground state is assumed to be 2A_1 . Here, ${}^2A_1 \rightarrow {}^2B_2$ and ${}^2A_1 \rightarrow {}^2E$ are z - and (x,y) -polarized, respectively. If the ground state corresponds to the irreducible representation 2B_1 , only the (x,y) -polarized transition ${}^2B_1 \rightarrow {}^2E$ is electronically allowed. Several models can be applied to explain this discrepancy to the experimental results, e.g. vibronic coupling of the first excited state into the ground state, a vibronic mechanism [5], or a superposition of V_{Zr} - and V_{Si} -induced absorption bands [7]. The observed EAS spectra with three $d-d$ -transitions cannot be explained by assuming vanadium to substitute for zirconium or silicon without one of these suggested assumptions.

As will be shown by quantum chemical calculations, the ground state of V_{int} in C_2 is of 2A symmetry and involves a single occupied d_{x^2} -orbital. Among the four transitions allowed there are two x -polarized ${}^2A \rightarrow {}^2A$ ones and two y - and z -polarized ${}^2A \rightarrow {}^2B$ transitions. Thus, in this case, more transitions are allowed than observed. So, two z -polarized ${}^2A \rightarrow {}^2B$ transitions are expected if the primary beam is polarized parallel to the crystal's main axis c . In case of polarization perpendicular to c , both two y -polarized ${}^2A \rightarrow {}^2B$ and

two x -polarized ${}^2A \rightarrow {}^2A$ transitions might be expected. However, it has to be kept in mind that the group theoretical approach does not give any information concerning the transition probabilities.

6. Quantum chemical calculations

The effect of the crystal field on the d -electron of V^{4+} is studied by means of quantum chemical configuration interaction (CI) calculations.

The chromophore was described by a single quantum chemically treated ionized vanadium atom embedded into a Madelung potential modelling the rest of the crystal. The Madelung potential was approximated by a set of about 500 point charges located at the usual structural sites occupied by the ions. The amounts of these charges were optimized by means of a least-squares fit with respect to the Madelung potential within a sphere of 4.5 Å radius around the vanadium atom. We used an atomic natural orbital (ANO) type basis [17] with a $(21s15p10d6f4g)/[8s7p6d5f4g]$ contraction scheme [18] equivalent to 194 primitive gaussians and 130 contracted functions. In correspondence to the lowest occurring site symmetry all calculations were done for C_2 symmetry. The orbitals were built by a doublet complete active space (CA) calculation with the first three roots equally weighted. The $1s$ orbital was frozen and the $2s$, $2p$, $3s$, $3p$ orbitals were kept inactive leaving one electron active within the 5 $3d$ -orbitals summing up to 19 electrons corresponding to a V^{4+} ion. In order to take dynamic correlation effects within the vanadium atom into account, we used a subsequent multi-reference configuration interaction (MR-CI) calculation employing the same reference space as before and left the $1s$, $2s$ and $2p$ orbitals frozen.

As the ionic radii of the substituting V^{4+} (0.86 Å, eight-fold coordinated ion, 0.65 Å, four-fold coordinated ion) differ from those of Zr^{4+} (0.98 Å, eight-fold coordinated ion) and Si^{4+} (0.40 Å, four-fold coordinated ion) [19], possible lattice relaxation effects due to incorporation are taken into account by scaling the first coordination sphere within a reasonable area. Hence, in V_{Zr} (4×2.12 , 4×2.27 Å), a reduction of the V–O bond lengths of the VO_8 -dodecahedron by a factor of 0.88 is likely to occur. In V_{Si} (4×1.63 Å), an expansion by a factor of 1.08 is expected, yielding V–O-bonds of 1.76 Å [6, 9, 10]. Finally, in V_{int} , only a slight distortion is to be assumed, since V^{4+} fits reasonably well into the available space with two distances of 1.76 Å and two of 2.02 Å.

The results of the CI-calculations bearing on the allocation problem of the dopant vanadium are shown in Fig. 3. Here, the energies of the transitions of either V_{Zr} , V_{Si} or V_{int} are plotted as functions of the scaling factor related to the changing mean V–O distances in the

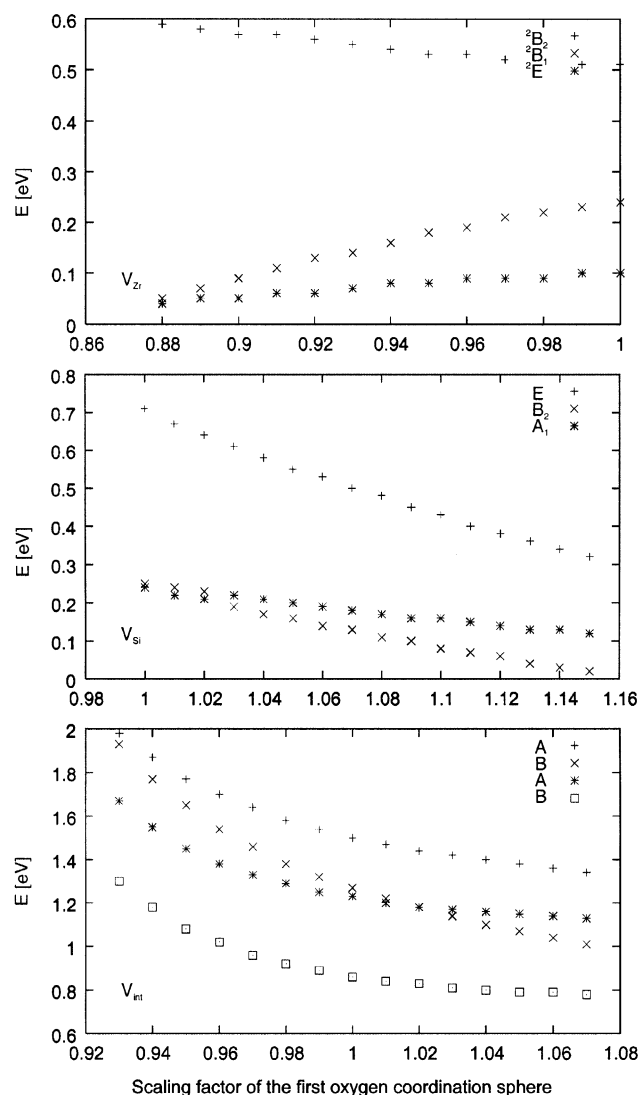


Fig. 3. The four lowest excitation energies for a V^{4+} ion embedded into a Madelung potential depending on the ligand field perturbation of the first coordination sphere. From top to bottom V_{Zr} , V_{Si} , V_{int} (cf. text).

respective polyhedron. The scaling in Fig. 3 is such that a factor of 1.00 represents the mean oxygen–metal distance of the V-free zircon.

7. Discussion

The calculated excitation energies obtained for V^{4+} at the V_{Zr} position lie in the IR region of the spectrum. The effect of the uniform decreasing of the V–O-distances is shown in Fig. 3. In Table 2 the excitation energies, their states and polarizations are shown for the scaling factors 1.00 and 0.88. The calculated transition energy ${}^2A_1 \rightarrow {}^2B_2$ rises on distance reduction. However, it remains much too low in comparison with the energy of the observed bands. Furthermore, the energy separations of the

Table 2

Excitation energies and oscillator strengths for a V^{4+} -ion inserted into the zirconium site (V_{Zr}) with the first oxygen coordination sphere distances scaled by a factor of 1.00 (left) and 0.88 (right)

State	Factor 1.00 E (eV)	$f(10^{-6})$		Factor 0.88 E (eV)	$f(10^{-6})$	
		$x=y$	z		$x=y$	z
2A_1	0.00	—	—	0.00	—	—
2E	0.10	0.02	—	0.04	0.04	—
2B_1	0.24	—	—	0.05	—	—
2B_2	0.51	—	0.12	0.59	—	1.3

observed absorption bands are not at all reproduced. Finally, with 2A_1 as ground state, the two electronically allowed transitions have the wrong polarizations with respect to the observed bands.

For V_{Si} , the calculated excitation energies lie in the NIR region. In Fig. 3 and Table 3 the effect of adjusting the V–O-distances is shown. Increasing the mean V–O distance in the first oxygen coordination sphere by 1.08 resulting in a realistic V–O-distance of 1.76 Å has the effect of further lowering the excitation energies. The ground state 2B_1 found is an agreement with ESR studies [5]. In this case only one (x,y)-polarized transition can be excited optically. Thus, neither a substitution for the zirconium position (V_{Zr}) nor for the silicon position (V_{Si}) can explain the observed absorption spectra of zirconblue without further assumptions. Both the excitation energies are too low and the number of allowed transitions is too small.

For vanadium at the interstitial site, V_{int} , the calculated excitation energies lie in the NIR and visible region. As to be expected, on lowering or enhancing the V–O-distance, the energy levels shift to higher, or lower, energies, respectively, see Fig. 3. In Table 4, the calculated excitation energies, their polarizations and transition probabilities are shown. The energy differences are in reasonably good agreement with the positions of the observed absorption bands even assuming the zircon lattice to remain undistorted. Furthermore, the large energy gap between the ground state 2A and the first excited state 2B corresponds very well to the observed spectrum. The low energy of the ground state can be explained by the strong distortion of the site from ideal tetrahedral symmetry. The polarizations of the calculated transitions correspond to the polarizations of the observed $d-d$ -transitions. The calculated oscillator strengths give a qualitatively correct picture of the observed intensities. Both calculated x -polarized ${}^2A \rightarrow {}^2A$ transitions are observed experimentally, whereas the electronically allowed y - and z -polarized ${}^2A \rightarrow {}^2B$ transition at 1.27 eV ($10,244 \text{ cm}^{-1}$) is not observable in either direction due to a too low transition probability into the 2B state. Also, the intensity of the y -polarized ${}^2A \rightarrow {}^2B$ transition

Table 3

Excitation energies and oscillator strengths for a V^{4+} -ion inserted into the silicon site (V_{Si}) with the first oxygen coordination sphere distances scaled by a factor of 1.00 (left) and 1.08 (right)

State	Factor 1.00 E (eV)	$f(10^{-8})$		Factor 1.08 E (eV)	$f(10^{-8})$	
		$x=y$	z		$x=y$	z
2B_1	0.00	—	—	0.00	—	—
2A_1	0.24	—	—	0.11	—	—
2B_2	0.25	—	—	0.17	—	—
2E	0.71	1.9	—	0.47	2.4	—

Table 4

Excitation energies and oscillator strengths for a V^{4+} -ion inserted into the interstitial site (V_{int}) with the first oxygen coordination sphere distances scaled by a factor of 1.00

State	Factor 1.00 E (eV)	$f(10^{-6})$		
		x	y	z
2A	0.00	—	—	—
2B	0.86	—	2.3	6.3
2A	1.23	2.0	—	—
2B	1.27	—	0.2	4.2
2A	1.50	27	—	—

is too low to be observed in the spectrum perpendicular to c . In both cases of allowed ${}^2A \rightarrow {}^2B$ transitions, the calculated oscillator strengths of the y -polarized transitions are significantly lower than that of the z -polarized transitions. This is due to the different environment in the x,y -plane and z direction of this interstitial site. The coordination sphere of V_{int} is shown in Fig. 4. In the internal x and y directions, the chromophore has zirconium and silicon as next neighbors, whereas in the z direction there are no other ions at similar distances. Therefore, the transition probabilities of the y and z -polarized ${}^2A \rightarrow {}^2B$ transitions are different. However, it must be stressed that the oscillator strengths are much more sensitive to the theoretical modelling than the calculated transition energies.

Please note that the electronic absorption spectra do not show any significant temperature dependence of the intensity [5]. This is in agreement with our explanation of the spectra on the basis of purely electronic $d-d$ transitions of V^{4+} .

This discussion shows that the model used in the calculations is suitable to discriminate between V_{Zr} , V_{Si} and V_{int} and to reproduce the experimentally observed data for V_{int} . In addition to our quantum chemical calculations presented here, we tried to apply the angular overlap model (AOM) to solve the problem. However, in the present case, we did not obtain convincing results concerning transition energies as well we could not distinguish among the three cases under

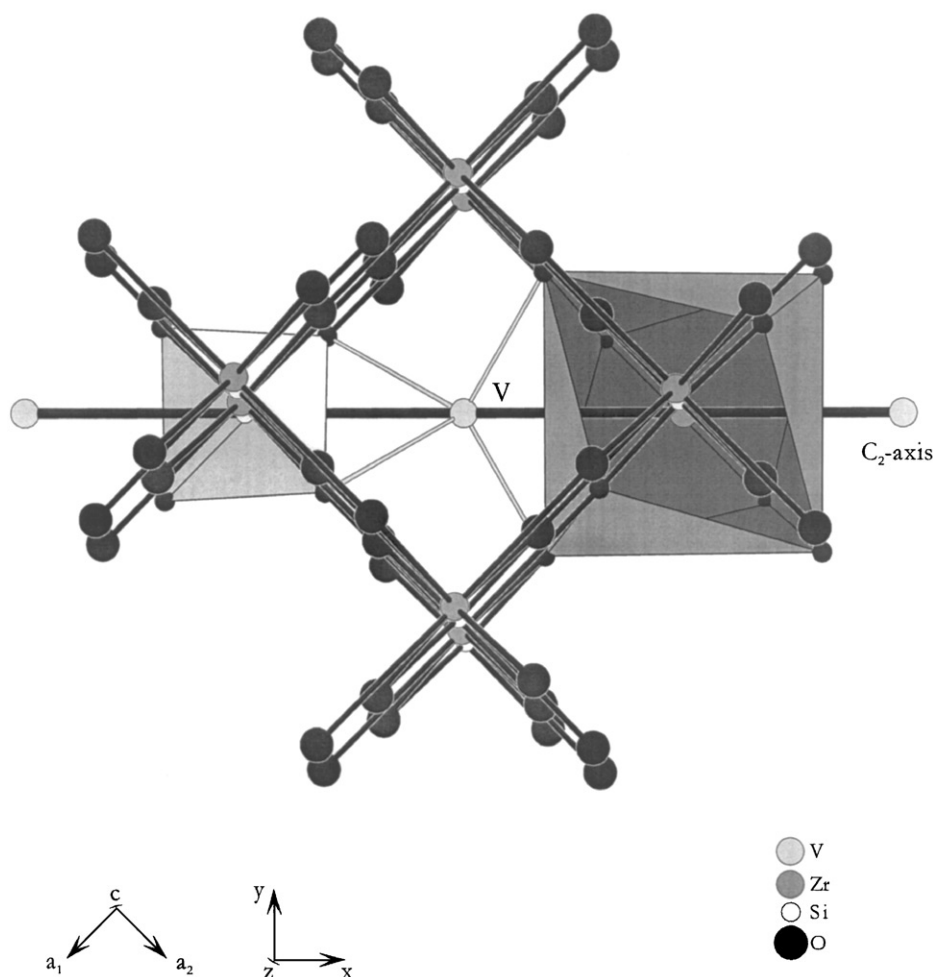


Fig. 4. Part of the tetragonal crystal structure of zircon along [001], showing the strongly distorted tetrahedrally coordinated interstitial site V_{int} .

discussion. Also, the AOM requires starting parameters (e_{σ} , e_{π}) and is always fitted to an experiment while the ab initio method we used is parameter free except for the structural parameters which are always necessary.

8. Conclusion

The direct comparison of the three cases of vanadium incorporation in zircon studies shows that the calculated excitation energies of V^{4+} if inserted into the zirconium or silicon sites (V_{Zr} , V_{Si}) are by far too low to explain the energies of the observed bands (cf. Fig. 3). In addition, the numbers of allowed transitions and the polarization directions (V_{Zr}) do not agree with the observed ones.

In contrast, the calculated excitation energies of V^{4+} at the interstitial site (V_{int}) are in close agreement with the observed $d-d$ -transitions of V^{4+} in zircon. Moreover, observed and calculated polarizations agree and the oscillator strengths are qualitatively correct. Therefore, we conclude that the observed absorption spectrum of zirconblue is explained by vanadium inserted into the

interstitial site. An additional substitution of zirconium and/or silicon cannot be excluded by the group theoretical or quantum chemical analysis done here. This is because the low-energy absorption bands predicted by the CI-calculations may occur at the calculated low energies in the IR region to which the measurements done so far have not been carried on.

However, the microprobe analyses of several crystals of zirconblue indicate clearly that a substitution for zirconium does not occur. The possible additional existence of V^{4+} on the silicon site should be established by polarized IR-measurements in the IR region up to 0.5 eV (4000 cm^{-1}).

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References

- [1] C.A. Seabright, US Patent 2441447, 1947.
- [2] C.A. Seabright, US Patent 3025178, 1962.
- [3] T. Demiray, D.K. Nath, F.A. Hummel, *J. Am. Ceram. Soc.* 53 (1970) 1–4.
- [4] A. Beltrán, S. Bohm, A. Flores-Riveros, J. Igualada, G. Monrós, J. Andrés, *J. Phys. Chem.* 97 (1993) 2555–2559.
- [5] S. Di Gregorio, M. Greenblatt, J.H. Pifer, M.D. Sturge, *J. Chem. Phys.* 76 (1982) 2931–2937.
- [6] D. de Waal, A.M. Heyns, G. Pretorius, R.J.H. Clark, *J. Raman Spectrosc.* 27 (1996) 657–662.
- [7] H. Xiaoyu, B. Gui-Ru, Z. Ming-Guang, *J. Phys. Chem. Solids* 46 (1985) 719–720.
- [8] M. Ocaña, A.R. González-Elípe, V.M. Orera, P. Tartaj, C.J. Serna, *J. Am. Ceram. Soc.* 81 (1998) 395–400.
- [9] P. Chandley, R. Clark, R. Angel, G. Price, *J. Chem. Soc. Dalton Trans.* 9 (1992) 1579–1584.
- [10] A. Siggel, M. Jansen, *Z. Anorg. Allg. Chem.* 583 (1990) 67–77.
- [11] K. Robinson, G.V. Gibbs, P.H. Ribbe, *Am. Mineral.* 56 (1971) 782–790.
- [12] K. Langer, in: E.K.H. Salje (Ed.), *Physical Properties and Thermodynamic Behaviour of Minerals*, Reidel, Dordrecht, 1988, pp. 639–685.
- [13] K. Langer, *J. Czech Geol. Soc.* 45 (2000) 37–62.
- [14] L. Cemic, S. Grammenopoulov-Bilal, K. Langer, *Ber. Bunsenges. Phys. Chem.* 90 (1986) 654–661.
- [15] MOLCAS Version 5. K. Andersson, M. Barysz, A. Bernhardsson, M.R.A. Blomberg, D.L. Cooper, T. Fleig, M.P. Fülscher, C. de Graaf, B.A. Hess, G. Karlström, R. Lindh, P.-Å. Malmqvist, P. Neogrády, J. Olsen, B.O. Roos, A.J. Sadlej, M. Schütz, B. Schimmelpfenning, L. Seijo, L. Serrano-Andrés, P.E.M. Siegbahn, J. Ståhring, T. Thorsteinsson, V. Veryazov, P.-O. Widmark, Lund University, Sweden, 2000.
- [16] M. Hanrath, B. Engels, *Chem. Phys.* 225 (1997) 197.
- [17] P.R. Almlöf, P.R. Taylor, *J. Chem. Phys.* 86 (1987) 4070.
- [18] R. Pou-Amérigo, M. Merchán, I. Nebot-Gil, P.-O. Widmark, B.O. Roos, *Theor. Chim. Acta* 92 (1995) 149.
- [19] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751–786.