EPR of VO^{2+} in the Mineral Wavellite $Al_3(OH)_3(PO_4)_2 \cdot 5\,H_2O$

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In wavellites from two different localities EPR spectra of VO^{2+} ions were detected and analyzed. The most prominent center was axial within the limits of error with $g = 1.932$, $g_{xx} = g_{yy} = 1.948$, $A_{zz} = 171.8$ and $A_{xx} = A_{yy} = 54.7$ (A in 10^{-4} cm). The orientation of the z-axis proves that the Al–OH group with the shortest Al–O bond is substituted by the VO^{2+} ion. Additional spectra of much lower relative intensity with different orientation of their z-axes can also be assigned to certain Al–O combinations.

Introduction

The VO^{2+} ion substitutes for a divalent cation in numerous synthetic crystals where simultaneous exchange of a water molecule against the O^{2-} ion results in perfect local charge compensation. The only known example of such a substitution in a mineral appears to be apophyllite $KCa(F, OH)Si_8O_{20} \cdot 8\,H_2O$ [1, 2]. Substitution of fourvalent titanium by VO^{2+} was observed in the mineral titanite (sphene) $CaTiOSiO_4$ [1, 3]. In this case the presence of one very short Ti–O bond in the domains with $P2_1/a$ space group [4, 5] undoubtedly favors incorporation of the vanadyl ion. The presence of several centers of VO^{2+} was reported for zoisite $Ca_2Al_3OHSi_3O_{12}$ [6]. In this case at least part of them must be incorporated in Al sites. Simultaneous exchange of the OH group against oxygen would again lead to perfect local charge compensation, and this indeed seems to occur for the center of highest concentration according to the orientations of the principal axes of its g and A matrices. There is also a brief remark about the occurrence of V^{4+} in amblygonite $LiAl(F, OH)PO_4$ where the same exchange is most likely, but no details were reported [7]. The same substitution is also possible in wavellite $Al_3(OH)_3(PO_4)_2 \cdot 5\,H_2O$, but the presence of two crystallographically inequivalent Al with two OH groups each in their first coordination spheres [8] at least in principle allows for the formation of up to four crystallographically inequivalent VO^{2+} centers. Thus this is a very suitable system for the study of structural details which govern this type of substitution.

Wavellite occurs in many localities as a secondary mineral in hydrothermal veins, in aluminous metamorphic rocks as well as in phosphate-rock deposits. It often occurs as aggregates of minute spherulithic crystals with c as their long axis. It crystallizes in the orthorhombic space group Pcmn, Al(1) has a monoclinic site symmetry with 2 O, 2 OH and 2 OH_2 as neighbors, whereas Al(2) with triclinic point symmetry is coordinated by 3 O, 2 OH and 1 OH_2 molecule [8]. These Al octahedra form chains along the c-axis, which explains the needle-like habit of the crystals. The average bond distance of Al(1) of 187 pm is significantly smaller than that of Al(2) of 191 pm.

Experimental

Wavellites from Montgomery County, Arkansas, USA and from Altmannsgrün near Ölsnitz, Saxonia, DDR were investigated. Both were yellow-green spherulithic aggregates from which small single crystals weighing between 10 and 20 mg were used for single-crystal investigations. EPR measurements were carried out at room temperature on an X-band spectrometer model ESP 300 10/12 of Bruker Analytische Messtechnik GmbH. Precise magnetic fields were determined using an NMR gaussmeter model ER 035 M of the same company, whereas microwave frequencies and spin concentrations were determined using

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piceine as standard [9]. Some EPR spectra were also recorded on model 414 and ER 200 D X-band spectrometers of the same company.

Results

In both powders and single crystals of specimens from both localities only one prominent EPR spectrum with $S = 1/2$ and octet hyperfine splitting (hfs) was observed. The powder spectrum in Fig. 1 suggests a practically axial site symmetry with too small differences between x and y to determine an orthorhombic component. The same result is obtained from single-crystal measurements with rotations around three mutually perpendicular axes, one of them the needle ($= c$) axis. In these measurements the z axis of highest hfs was found to coincide with the c axis within the limits of error of about 2°. The spectrum for this orientation is shown in the upper part of Figure 2. The linewidths were near 1.3 mT. From these single-crystal spectra the following results were obtained:

$$g_{zz} = 1.932(1);\ g_{xx} = g_{yy} = 1.948(1);$$
$$A_{zz} = 171.8(2);\ A_{xx} = A_{yy} = 54.7(3)10^{-4} \cdot cm^{-1}.$$

Within the limits of error these values agree with those obtained in a simulation of the powder spectrum of Figure 1.

A splitting of up to 2 mT was observed in a rotation around an axis perpendicular to the c axis at orientations intermediate between B_0 parallel and perpendicular to the c axis.

Presence of additional centers in much lower concentrations with the same octet hfs is evident from the lower spectrum in Figure 2. The relative concentrations of these octets are between 3 and 5% of that of the main spectrum. This spectrum may suggest that both g_{zz} and A_{zz} for one of these centers are practically equal to those of the main center, and that they may be caused by very small crystals attached to the main one with their c axes oriented at right angles to that of the main one. However, in enlarged powder spectra of samples from both localities small additional signals occur between the intense outer ones for z of the main center. Thus A_{zz} for them is significantly smaller, and their outermost components in the lower spectrum of Fig. 2 cannot belong to the same center. From this powder spectrum the following combinations of pa-

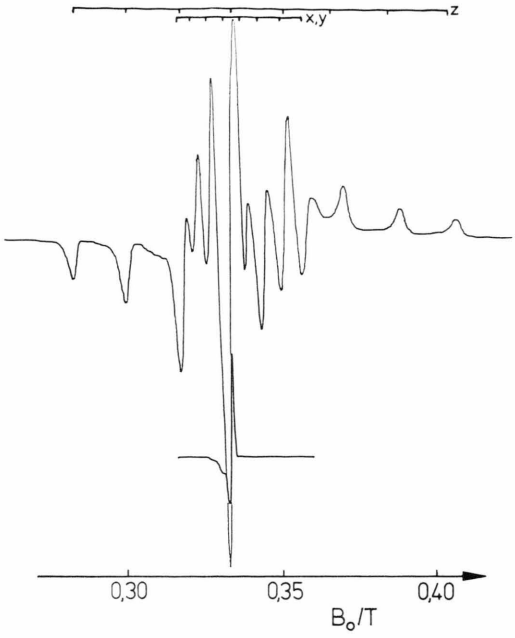

Fig. 1. Powder EPR spectrum of wavellite from USA at 9.4 GHz and room temperature. The lower signal is due to piceine as standard.

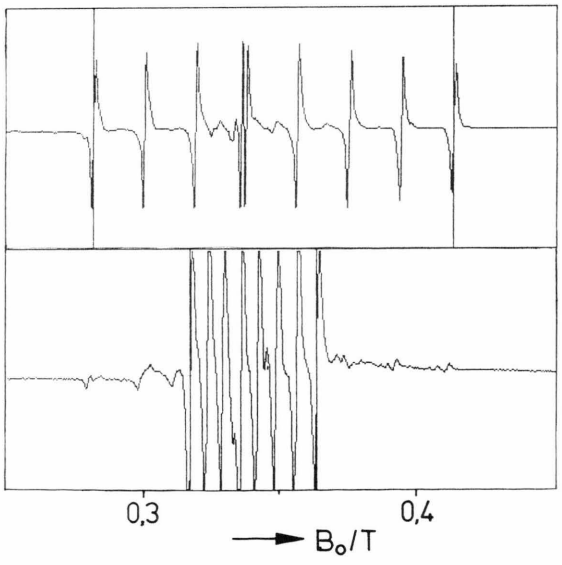

Fig. 2. EPR spectra at 9.4 GHz and room temperature for a single crystal of wavellite from USA. Upper spectrum: $B_0 \parallel c$. The additional signal preceding the fourth hfs component is due to piceine as standard, the smaller signals close to it most likely arise from other paramagnetic species than V^{4+}. Lower spectrum: $B_0 \perp c$. The small signals on both sides of the intense octet are due to other centers of VO^{2+} present in much lower concentrations.

rameters were obtained for two centers of low intensity:

g_{zz}		$A_{zz}/10^{-4}\,cm^{-1}$
1.939 and 1.955		150 and 150
	or	
1.944 and 1.949		151 and 147

Measurement of the spin concentration using piceine as standard [9] resulted in a concentration of 0.7% spins per formula unit for a sample from USA. The concentration in the crystals from DDR must be very similar according to the similar signal/noise ratios in the EPR spectra of samples of comparable weight and to the similar intensities of the yellow-green colors.

Discussion

The structures of the observed paramagnetic centers and the structural details causing highly preferred formation of one center only will be considered first. Then the spin Hamiltonian parameters will be analyzed and the results compared with those for zoisite, the only other system for which substitution of Al sites by the same type of centers was reported.

Structure of Centers

The pronounced anisotropy of the hyperfine splitting with a several times larger value of A_{zz} and the principal values of g with the lowest value for g_{zz} are characteristic for the d^1 ion VO^{2+}. Their absolute values are also in good agreement with data for the same ion in other minerals which are listed in Table 1.

Table 1. Spin Hamiltonian parameters for VO^{2+} in minerals.

Mineral	g_{zz}	$\frac{g_{xx}+g_{yy}}{2}$	A_{zz}*	$\frac{A_{xx}+A_{yy}}{2}$	Ref.
Apophyllite**	1.933	1.947	180.2	60.6	2
	1.948	1.96	166.2	59	
Titanite	1.943	1.958	174.3	54.8	3
Zoisite	1.948	1.955	163.4	51.2	6
	1.938	1.936	161.7	48.8	
	1.876	1.981	155.5	61.6	
	1.934	1.944	163.7	52.9	
Topaz	1.950	1.926	160	141	17)
$Al_2F_2SiO_4$	1.914	1.932	153	139	
Garnet	1.856	1.979	137.4	29.8	18)

* A_{ii} in $10^{-4}\,cm^{-1}$. ** In Ca and K sites resp.

The almost equal amplitudes of all eight hfs components in the upper single-crystal spectrum of Fig. 2 indicate absence of inhomogeneous broadening due to a large distribution of hfs constants which would lead to excess broadening of the outer components as observed in a number of systems including garnets [10], zircon [11], apophyllite [2] and synthetic crystals [12]. Most likely unresolved hfs splitting due to the ^{27}Al and ^{31}P nuclei in the neighborhood of the VO^{2+} contributes to the observed linewidths. Thus the ions appear to be present in well crystallized surroundings.

Since the z axis of the VO^{2+} at least approximately coincides with the V=O bond direction, its orientation should allow assignment of the prominent center to one of the four crystallographically inequivalent Al–OH groups in the structure of wavellite. An excellent agreement with the Al(1)–OH(1^3) direction (notation as in [8]) is observed for this center: It is only 1.2° away from the c-axis, and due to the C_s site symmetry with the Al(1)–OH(1^3) group in the mirror plane the b axis is one of the principal axes of a VO^{2+} ion substituting it. This is the shortest of the four Al–OH bonds. Thus these results suggest that the possibility of formation of the shortest V=O bond is energetically preferred and that preponderance of one configuration is determined by equilibrium, not by kinetic factors during crystal growth. Assuming a growth temperature near 400 K, an energy difference in the range of 10 kJ/mol is obtained from the intensity ratios of about 25 relative to the centers of low intensity. A possible difference in entropy should be negligibly small. Thus, as a consequence of the most likely rather low growth temperatures small energy differences are already sufficient to cause a strong preference for one configuration. In principle it should be possible to determine differences in growth temperatures from variable intensity ratios in samples from different localities. However, for the two wavellites studied here these ratios were very similar.

Since the smaller Al site with an average bond distance of 187 pm compared to 191 pm for Al(2) is occupied by the vanadium impurity, this result is surprising: For other transition-metal ions like Mn^{2+}, Fe^{3+} and Cr^{3+} a strong preference for the larger site of a smaller host ion minimizing the size mismatch is usually observed [13].

The splitting of up to 2 mT can be explained by the lower than axial site symmetry. It is expected for rotation around the b-axis as soon as the other two prin-

cipal axes do not perfectly coincide with the *a* and *c* axes. It can easily be verified that the main cause of this splitting should be the anisotropy of *A*, and indeed a maximum splitting of the observed magnitude can be estimated for the postulated difference in orientation of the order of 2 to 3°.

Since the other three Al−OH bonds are about 20° inclined to the *c* axis, they can be excluded for this prominent as well as for the centers of low concentration with their *z* axes almost perpendicular to the *c* axis. The Al(1)−O(2) bond with an angle of about 80° to the *c* axis has a suitable orientation to be assigned to one of these centers. Again this is by far the shortest of the three Al−O bonds. Substitution by VO^{2+} would result in two magnetically nonequivalent triclinic centers. This center could arise from the same coupled substitution of Al(1)−OH(1^3) by V−O and a subsequent valence isomerism, but this seems unlikely in view of the large initial difference of bond lengths of about 6 pm. Another, more likely possibility would be a coupled substitution of an Al−O−P group by V=O··Si which again results in perfect local charge compensation. The Al(1)−OH_2(1) bond with a bond length of 198.4 pm has a similar orientation, and in this case a coupled substitution of Al−OH_2··P by V=O···S would result in perfect local charge compensation. In both cases the symmetry would be lowered to triclinic. A statistical charge compensation for either one of these possibilities cannot be excluded. Within the limits of error the bond lengths of the two Al−OH_2 groups of Al(1) and Al(2) are the same.

The significantly smaller values of A_{zz} for these centers of lower intensity are a clear indication of larger V=O bond distances. Although a quantitative correlation between A_{zz} and the V=O bond distance is still lacking mainly because this center is almost always observed as an impurity for which the precise geometries are not known, results for α−$VOPO_4 \cdot 2H_2O$ [14] indicate that a value of A_{zz} near $174 \cdot 10^{-4}$ cm^{-1} corresponds to a V=O bond length near 160 pm. Thus the V=O bond length for the prominent center should be only slightly larger and considerably shorter than the original Al(1)−OH(1^3) bond. On the other hand, in sites which due to a center of symmetry do not favor formation of one short bond like in the rutile structures of TiO_2 and SnO, considerably smaller values of A_{zz} of only 141 and $128 \cdot 10^{-4}$ cm^{-1} resp. [15] are observed, much smaller than for the centers of low symmetry.

Analysis of EPR data

From the principal values of *g* and *A* the isotropic part *K* and the dipolar term *P* of the hfs splitting can be calculated according to

$$A_{\parallel}\,(=A_{zz}) = K \cdot \alpha^2 + P(-\tfrac{4}{7}\alpha^2 + \Delta g_{\parallel} + \tfrac{3}{7}\Delta g_{\perp})$$

and

$$A_{\perp} = K\alpha^2 + P\,(\tfrac{2}{7}\alpha^2 + \tfrac{11}{14}\Delta g_{\perp})\,.$$

Since only two constants can be calculated from these two equations, $\alpha = 1$ (the purely ionic limit) was assumed, a reasonable approximation. It results in $K = -86.0$ and $P = 128.9$ (both in units of 10^{-4} cm^{-1}). Both are in the range normally observed for VO^{2+} ions [16], the negative sign for *K* is expected for dominant exchange polarization as usually assumed for this ion. A lower value of α increases both *K* and *P* accordingly.

From

$$\Delta E_1 = -\frac{8\lambda}{\Delta g_{\parallel}} \quad \text{and} \quad \Delta E_2 = -\frac{2\lambda}{\Delta g_{\cdot}}$$

with λ the spin-orbit coupling constant of about 150 cm^{-1} the positions of the two ligand field bands of lowest energy corresponding to excitation of the unpaired electron from the d_{xy} to the $d_{x^2-y^2}$ and d_{xz}, d_{yz} levels resp. can be estimated. The resulting values of 17000 and 5500 cm^{-1} are again in the usual range. The first one is in the visible range, and the position of this band determines the color resulting from presence of VO^{2+}. The green color observed in the wavellite as well as in titanites [2], apophyllite [3] and zoisite with content of VO^{2+} [6] show that its position apparently does not vary significantly although in apophyllite a bluish-green instead of a yellow green hue was observed.

Comparison with VO^{2+} in zoisite

In this case only one Al−OH group is present, but four crystallographically nonequivalent centers of VO^{2+} were observed [6]. Two of these with low intensity could only be detected at low temperatures, a result normally observed in fourfold coordination due to increased relaxation times as a consequence of lower energy differences to the excited states. Thus these centers may arise from substitution of Si sites. The *z* axis of the triclinic center of VO^{2+} very nearly has the

same direction as the Al(1)—OH bond [16], the agreement is much better than with the Al(1)—O(4) bond which is the shortest one for the triclinic Al(1) site and the one proposed by Hutton [6] for this triclinic (site 1) center. Thus once again a substitution of an Al—OH group against V=O can be assumed. The second center of monoclinic site symmetry with its z axis close to the a axis was assigned to substitution of Al(3)—O(8) by V=O by the author. Again this is the shortest Al—O bond of Al(3), and thus the result is reasonable, but Al(3)—O(4) also cannot be excluded as the site of the V=O group. In this case a coupled substitution of Al—O—Si against V=O··Al would lead to perfect local charge compensation.

In topaz the z axis of one center coincides with the direction of the shortest Al—F bond [17] indicating exchange of this fluorine by the oxygen of the VO^{2+} ion.

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