Electron Paramagnetic Resonance and Optical Absorption Spectra of VO^{2+} in CsCl Single Crystals

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In vanadium-doped CsCl crystals grown from aqueous solutions anisotropic EPR spectra due to VO^{2+} are observed and analyzed at room temperature. Evidence is presented that isotropic spectra of this ion observed in this and other compounds are due to inclusions of growth solution and not to rapid rotation of the vanadyl ion in the solid as normally assumed. At 77 K a well resolved vibrational progression of about 820 cm^{-1} is observed in the first ligand field band of this ion. The optical absorption spectra indicate the presence of a second valence state of vanadium, most likely V^{3+}, in varying proportions depending on the crystal growth temperature.

Introduction

EPR studies of VO^{2+} in doped single crystals have been reported for a large number of systems [1–15]. The observed anisotropy led to conclusions about the location and geometry of this ion in the lattice in question. In particular the strong anisotropy of the ^{51}V hyperfine coupling as a consequence of the short V=O bond distance, aided in these assignments. In a large number of compounds, however, including NH_4NO_3, $NaNO_3$ and $Ba(NO_3)_2$ [10], KNO_3 and $CsNO_3$ [11], KBr and KI [12], NH_4Cl [14], $BaCl_2 \cdot 2\,H_2O$ [15, 16], $BaBr_2 \cdot 2\,H_2O$ [16], NaCl, RbCl [17] and CsCl [17 a] no preferential orientation could be detected. At room temperature isotropic spectra were observed in these systems and the linewidths of the eight hyperfine components varied with the quantum number m_I according to

$$\frac{1}{T^2} = \pi \sqrt{3}\,(a_1 + a_2\, m_I + a_3\, m_I^2) \quad [18] \qquad (1)$$

in agreement with the theoretical predictions [19]. At low temperatures spectra typical of random orientation of anisotropic species as usually observed in powdered crystals or glasses were found. These results were interpreted in terms of rapid rotations of the vanadyl species at room temperature and static random orientations at low temperatures.

We have also observed such isotropic spectra in a number of additional compounds. Closer inspection strongly supports a completely different explanation, namely the presence of liquid inclusions of the growth solutions in these crystals. Finally, in CsCl single crystal spectra were observed at room temperature lending additional support to our interpretation of the isotropic spectra.

Experimental

EPR measurements were carried out on commercial X- and Q-band spectrometers, B-ER 414s and B-ER 420 Q, respectively, of Bruker Analytische Meßtechnik GmbH., Karlsruhe. Low temperature spectra were obtained at X-band using a CSA-202 Cryogenic Refrigeration System of Air Products and Chemicals, Inc., Allentown. UV-VIS spectra were measured on a Perkin-Elmer spectrophotometer model 330 at room temperature and 77 K using a cryostat filled with liquid nitrogen. Infrared spectra were recorded on a Beckmann Acculab 8.

Results and Discussion

EPR

Isotropic EPR spectra due to VO^{2+} were observed in $Cs_3Sb_2Cl_9$, $CsGaCl_4$, $CsGaBr_4$ and $(CH_3NH_3)_3SbCl_6$ grown from acidified aqueous solutions containing 1 mole% of vanadium per trivalent cation added as V_2O_5 and reduced by addition of small amounts of ethanol. At 20 K anisotropic spectra of randomly oriented VO^{2+} were found in $CsGaBr_4$. The results are listed in Table 1 together with data for solutions from the literature.

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Table 1. EPR parameters of VO^{2+} in fluid inclusions and solutions.

System	298 K		20 K			
	g	$A/10^{-4}\,\mathrm{cm}^{-1}$	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
$CsGaBr_4$	1.967	108 ± 1	1.929	1.984	182	71
$CsGaCl_4$	1.964	107 ± 1				
$Cs_3Sb_2Cl_9$	1.966	106 ± 1				
$(CH_3NH_3)_2SbCl_6$	1.965	107 ± 1				
				77 K		
HCl pH ≈ 2 [20]	1.963	108	1.933	1.978	182.6	70.7
$3n$ HCl [21]	1.965	106.4	1.932	1.981	182.6	71.8

Table 2. EPR parameters of oriented VO^{2+} in single crystals.

Compound		g_x	g_y	g_z	A_x*	A_y	A_z	Ref.
$(NH_4)_2Zn(SO_4)_2 \cdot 6\,H_2O$	I	1.9813	1.9801	1.9331	71.4	72.6	182.2	[1]
	II	1.9808	1.9797	1.9316	71.0	72.6	182.8	
$Cs_2C_2O_4 \cdot H_2O$		1.977	1.978	1.9344	68.5	67.1	175.2	[4]
$Mg(H_2O)_6H_2EDTA$	I	1.977	1.991	1.939	60.0	67.3	175.4	[5]
	II	1.979	1.985	1.936	62.0	65.6	173.5	
$(NH_4)_3H(SO_4)_2$		1.976	1.973	1.917	67.6	69.7	182.7	[7]
$Ba_2Zn(HCOO)_6 \cdot 4\,H_2O$		1.974	1.979	1.943	60.7	59.7	166.5	[6]
$(NH_4)_2InCl_5$		1.9847		1.9450	63.8		173	[3]
$(NH_4)_3AlF_6$		1.977		1.937	64.5		178.5	[8]
$(NH_4)_2SbCl_5$		1.9793		1.9478	62.8		168.8	[13]
CsCl		1.980 ± 0.001	1.979 ± 0.001	1.9342 ± 0.0005	67 ± 2	71 ± 2	180 ± 1	this work

* all A_i in units of $10^{-4}\,\mathrm{cm}^{-1}$.

Clearly the results for the crystals are very similar to those of the solutions suggesting that in the crystals inclusions of the growth solutions may be present. This conclusion is in fact supported by further evidence, namely

(i) All crystals exhibiting isotropic spectra were grown from solutions.

(ii) In crystals of $CsGaCl_4$:VO^{2+}, grown from D_2O, the linewidths are smaller than in the same crystals grown from H_2O solutions, suggesting coordination of the VO^{2+} species by water molecules.

(iii) For rapidly rotating VO^{2+} species identical spectra should result in single crystals and powders. This is not true for the compounds in Table 1. After crushing to a fine powder and drying in vacuum these crystals showed only slightly structured signals near $g = 2$. We interpret this as evidence for crystallization of highly concentrated VO^{2+} species due to evaporation of the solvent water.

(iv) It is unlikely that the proposed rotation of VO^{2+} in significantly different compounds could always be quenched to a completely random orientation. Instead, at most, a few preferential orientations should be strongly favored energetically and thus the spectra should change with orientation of the crystal.

(v) The parameters a_i, describing the dependence of linewidths on m_I in (1), vary in solution with VO^{2+} concentration [20] in an analogous manner to that reported for different host compounds. Different VO^{2+} concentrations in the liquid inclusions, on the other hand, can be due to different doping levels as well as variable solubilities of the host compounds.

(vi) There is no reason why the dynamical properties of the vanadyl species should vary drastically in systems with very similar chemical and structural properties like the alkali halides. While in all alkali

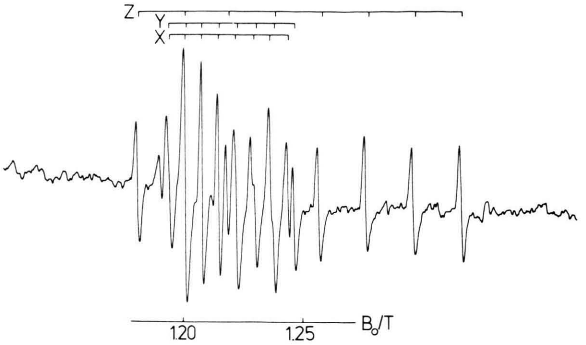

Fig. 1. EPR spectrum of VO^{2+} in a CsCl single crystal at Q-band (33.77 GHz) and 298 K for B_0 parallel to one of the fourfold crystal axes.

halides (including CsCl) studied so far isotropic spectra were observed at room temperature we found anisotropic, single crystal spectra for CsCl crystals grown from aqueous solutions doped with 1 mole% of vanadium as is also observed for the halide systems $(NH_4)_2InCl_5$ [3], $(NH_4)_3AlF_6$ [8] and $(NH_4)_2SbCl_5$ [13]. Two examples of these spectra are shown in Figs. 1 and 2, while Fig. 3 shows the angular variation for rotation around a fourfold crystal axis. The numerical results obtained from these measurements are listed in Table 2 together with those for other compounds with anisotropic single crystal spectra from the literature. For CsCl a very slight rhombic distortion in addition to a large axial one was obtained. Most likely the VO^{2+} is aligned along the fourfold crystal axes with the vanadium between two empty Cs sites with an additional water molecule near the empty Cs site opposite to the vanadyl oxygen. For such a $[VO(OH_2)Cl_4]^{2-}$ unit a C_{4v} point symmetry would be expected. Thus the origin of the small rhombic distortion remains an open question. In our view hydrogen bonding of the water molecule to two Cl^- is the most likely cause. The dashed lines in Fig. 3 are of low intensity and may be caused by a second center with very similar hyperfine coupling constants. This may be the complex $[VOCl_4]^{2-}$ having slightly different g-factors.

Optical Absorption

CsCl crystals used for these optical absorption measurements were grown from solutions with 5 mole% of vanadium. Spectra were recorded at both

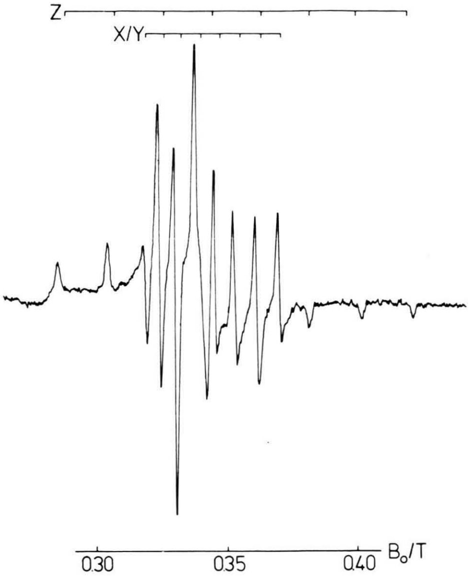

Fig. 2. EPR powder spectrum of $CsCl:VO^{2+}$ at X-band (9.55 GHz) and 298 K.

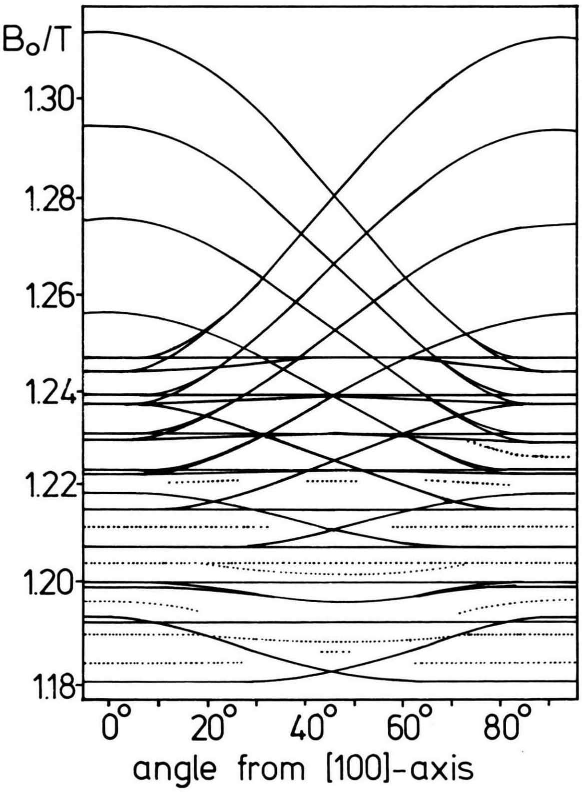

Fig. 3. Angular variation of the EPR line positions at Q-band and room temperature for VO^{2+} in CsCl. The dashed lines are of lower intensity and may be due to a second center.

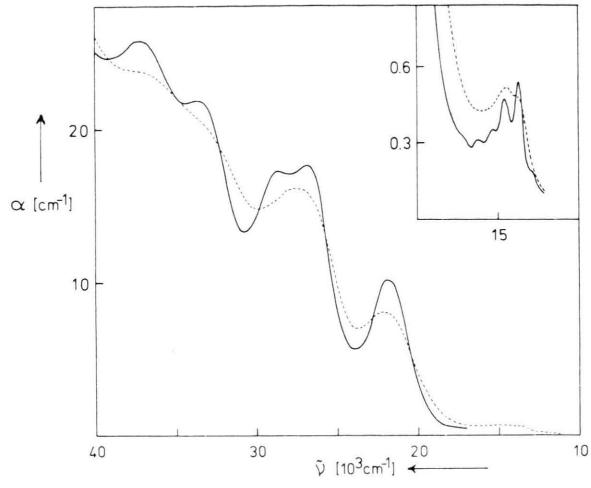

Fig. 4. Optical absorption spectra of a vanadium-doped CsCl single crystal at 298 (– – –) and 77 K (——).

Table 3. Absorption maxima (in cm^{-1}) and assignments for CsCl : V and Cs_2VOCl_4

CsCl			Cs_2VOCl_4	
298 K	77 K			
	12930	$^2B_2 \rightarrow {}^2E$	13900	$^2B_2 \rightarrow {}^2E$
13640	13740			
14460	14570			
	15400			
	16200			
	17010			
	17890			
22000	21800		24000	$\rightarrow {}^2A_1$
27500	26800			
	28700	(V^{3+} ?)	29000	charge transfer
32800	33600	charge transfer	32400	
36700	37300		37800	
			41600	
			45500	

room temperature and 77 K. Results for an orange-colored crystal grown at room temperature are shown in Figure 4. As shown in Table 3, six distinct bands are resolved at room temperature. Particularly the ones at lowest energy split up into still more components. These bands do not, however, all originate from the same center since at higher growth temperatures in the range of 50 to 60 °C green crystals result in which the lowest energy bands are about five times as intense whereas the next three bands at higher energies are lower and the two bands at highest energies could not be measured due to too high absorption in this range.

The band system starting at about 13 000 cm^{-1} undoubtedly arises from the VO^{2+} ion and can be assigned to the $^2B_2 \rightarrow {}^2E$ ligand field transition normally observed in this region. Higher ligand field transitions (to the $^2B_1$ and $^2A_1$ states) are expected near 16 000 and 30 000 cm^{-1} respectively. The latter may be obscured by the much more intense first charge transfer band expected at or below 41 000 cm^{-1} depending on the electronegativity of the ligands. The band system starting at 13 000^{-1} shows a well resolved vibrational progression of about 820 cm^{-1} at 77 K, the two most intense components are already resolved at room temperature. A vibration at 990 cm^{-1} in this crystal can be interpreted as the V=O stretching mode which occurs at practically the same position in $Cs_2VOCl_4 \cdot H_2O$ [22] and $VOCl_2 \cdot x\,H_2O$ [23]. Occupation of the e_π^* orbital in the excited state leads to a weakening of this bond and thus at least qualitatively explains the distinctly lower wavenumber of the progression. The positions of all bands in CsCl are compared to those in Cs_2VOCl_4 from the literature [24]. The band positions in the diffuse reflectance spectrum of this compound are very similar to those of $Cs_2VOCl_4 \cdot H_2O$ [22, 24]. The two highest energy bands near 33 000 and 37 000 cm^{-1} in CsCl most are likely charge transfer transitions whereas the bands in the range of 22 000 to 29 000 cm^{-1} must be due to another species. Their most likely cause is V^{3+} which cannot be detected by EPR at room temperature, attempts to detect it at 20 K were also unsuccessful. Three ligand field transitions are expected for this ion in cubic symmetry. The first two occur at 17 800 and 25 700 cm^{-1} in $NH_4V(SO_4)_2 \cdot 12\,H_2O$ [25, 26]. The somewhat different positions in CsCl may be due to the different coordination and/or lower site symmetry. The results for Cs_2VOCl_4 listed in Table 3 suggest that an additional band of the VO^{2+} ion may also be present near 29 000 cm^{-1}, but most likely strongly overlapped by an absorption band of the V^{3+} species. Incorporation of another trivalent transition metal ion, namely Cr^{3+}, in CsCl has been demonstrated by both EPR and optical absorption measurements [27].

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