Strong-field matrices of $d^4(C^*_{3v})$ and optical-magnetic property studies on XCrCl$_3$ (X = Cs, Rb)

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Strong-field matrices of $d^4(C^*_{3v})$ and optical–magnetic property studies on $XCrCl_3$ (X = Cs, Rb)

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Abstract. Making use of the strong-field matrices of $(C^*_{3v})d^4$ in the O^*_h point group representation, the absorption spectra of $XCrCl_3$ (X = Cs, Rb) crystals have been systematically analysed. The main crystal-field parameters can be determined from the observed spin-allowed absorption bands. The spin forbidden absorption bands for $\Delta S = 1$ are calculated and the zero-field splitting of the ground state is obtained theoretically. The complicated absorption spectra of both crystals $XCrCl_3$ are carefully analysed after considering the vibronic coupling with vibrational progressions of $100\ cm^{-1}$ (Cs) or $50\ cm^{-1}$ (Rb) and the double d excitation induced by exchange coupling between Cr^{2+} spins and the spin–spin interaction splitting in $XCrCl_3$ crystals. Finally, the g-factor is calculated by use of the ground-state EPR induced by the Jahn–Teller effect of Cr^{2+} and the optical–paramagnetic properties of $Cs(Rb)CrCl_3$ are explained in detail by comparing the calculated result with experiment.

1. Introduction

The structural phase transitions in $CsCrCl_3$ and $RbCrCl_3$ crystals induced by the Jahn–Teller effect of the Cr^{2+} ion have been well discussed and analysed (McPherson *et al* 1972, Tanaka *et al* 1983, 1986, Bastow and Whitefield 1980). Tanaka *et al* (1983) and Tazuke *et al* (1984) have measured the magnetic susceptibilities of $Cs(Rb)CrCl_3$ and after analysis of the interchain exchange interaction the temperature dependence of the antiferromagnetic property of $Cs(Rb)CrCl_3$ is determined. The g-values determined by this method are consistent with those determined by EPR within the experimental error (Tazuke *et al* 1984). Although the exact observed results of polarisation absorption spectra for $Cs(Rb)CrCl_3$ crystals have been obtained (McPherson *et al* 1972, Alcock *et al* 1976, Grama *et al* 1978), as indicated by Tazuke *et al* (1984), however, a reasonable theoretical analysis of the details of the spin-forbidden absorption spectra has not been established.

For example, it is shown from the spectrum of $CsCrCl_3$ that there are three sets of strong peaks gathering in the neighbourhood of $6500\ cm^{-1}$ and $22\,300\ cm^{-1}$ respectively (Alcock *et al* 1976). In the O_h symmetry approximation the spin-allowed transitions among the spin quintets in the neighbourhood of the $6500\ cm^{-1}$ band will not appear, so the strong band at $6500\ cm^{-1}$ is assigned a spin-forbidden band by Li and Studky (1973) and Alcock *et al* (1976). But it is shown from the oscillator strengths and the shape of the spectral diagram that the absorption peak in the neighbourhood of the $6500\ cm^{-1}$

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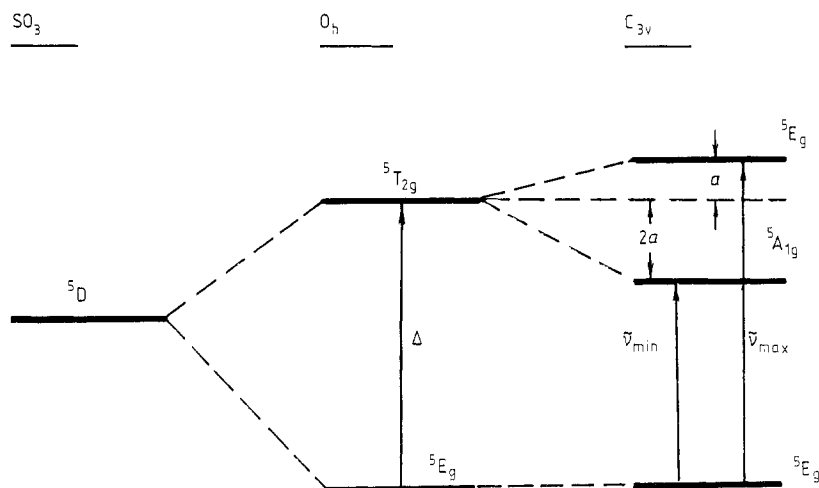
Figure 1. The energy level splitting of d^4 in the C_{3v} crystal field.

band should be a typical spin-allowed transition, superposed with some spin-forbidden bands (McPherson *et al* 1972). As indicated by the method of König and Kremer (1974), the complicated structure of the absorption spectra gathering in the regions covering 16000–25000 cm^{-1} cannot be explained even if a crystal field with O_h symmetry and the spin–orbit interaction are considered simultaneously. Because the structural distortion of the $CrCl_6^{4-}$ complex in both crystals induced by the Jahn–Teller effect of Cr^{2+} and its surroundings is large, Li and Studky (1973) and Alcock *et al* (1976), have determined, using x-ray diffraction, that the $CrCl_6^{4-}$ octahedral complex ions sharing faces to form linear chains have C_{3v} distortion. Therefore, in order to explain the complicated structures in the spectra, Alcock *et al* (1976) indicated that the influence of both spin–orbit coupling and the C_{3v} symmetry of the crystal field should be considered simultaneously. Otherwise, the paramagnetic *g*-factor cannot be calculated using any theory. It is also well known that theoretical calculations for the paramagnetic *g*-factor and the zero-field splitting of the ground state are helpful in understanding optical and magnetic properties.

The purpose of this paper is to build up the complete strong-field matrices of $C_{3v}^*(d^4)$ (here and below the symbol * denotes a spin–orbit product group) on the basis of an O_h^* point group representation strong-field scheme (Zhao *et al* 1986, 1989), and explain the optical spectra and the ground-state zero-field splitting of Cr^{2+} by means of the eigenvalues. Finally, the paramagnetic *g*-factor of the group state of Cr^{2+} induced by the Jahn–Teller effect will be calculated.

2. Energy matrices

When there is no extra magnetic field, the Hamiltonian of a $Cr^{2+}(d^4)$ ion in a C_{3v} crystal field can be written as

$$H = H_0 + H_e + V_{so} + V_L$$

where $H_0 = \Sigma_i[(-\hbar^2/2m)V_i^2 + U(r_i)]$ with V_i and $U(r_i)$ the kinetic energy and the potential energy, respectively, of all the electrons in the field of the atomic nucleon; $V_e = \Sigma_i e^2/r_{ij}$ is the Coulomb interaction between pairs of electrons; $V_{so} = \Sigma_i \zeta(r_i)(s_1 \cdot L_1)$ is the operator of the spin–orbit interaction and $V_L = \Sigma_i U_{LF}(r_i)$ may be considered as a

Table 1. The spectrum analysis of the XCrCl$_3$ (X = Cs, Rb) spin quintet.

C$_{3v}^*$	Calculated $\Delta S = 0$ Band (cm^{-1})		Observed (cm^{-1}) (Alcock et al 1976, Grama et al 1978)		O$_h$(calculated) (Alcock et al 1976)	
	Cs	Rb	Cs	Rb	Cs	Rb
A$_1'$(1)	0	0			0(^{5}E)	0(^{5}E)
E'(1)	2.117	1.886				
A$_2'$(1)	5.876	3.530				
E'(2)	6.142	3.964				
E'(3)	6.973	4.316				
A$_1'$(2)	8.173	5.067				
A$_2'$(2)	10.248	6.456				
E'(4)	6261.5	6717	6250	6580		
E'(5)	6262.4	6718				
A$_1'$(3)	6340.4	6778	6490	6710		
A$_2'$(3)	11398	11658				
E'(6)	11401	11649				
A$_1'$(4)	11467	11701				
E'(7)	11515	11739	11500	11700	11500(^{5}T$_2$)	11700(^{5}T$_2$)
E'(8)	11571	11782		11730		
A$_2'$(4)	11628	11827				
A$_1'$(5)	11658	11850	11630			
2A$_2'$(4)	23256	23400	23228	23255		
2A$_1'$(5)	23316		23310			
Parameters (cm^{-1})	$\Delta = 9750$ $a = 1750$ $b = 41$ $\xi = 230$	$\Delta = 10056$ $a = 1673$ $b = 41$ $\xi = 180$			$\Delta = 11500$	$\Delta = 11700$

sum of four one-electron ligand field potentials. $H_0 + V_e + V_{so}$ is usually dealt with in terms of the central field approximation. For the Hamiltonian H we can build up matrices under the Γ' irreducible representation basic functions of d^4(C$_{3v}^*$), through an O$_h$ point group representation, by a block-diagonal scheme (Zhao *et al* 1986, 1989). In these matrices the matrix elements V_e distribute within each $S\Gamma$ term block and are expressed by Racah parameters A, B and C (Griffith 1961); the matrix elements V_{so} distribute within each Γ'(O$_h^*$) block and are expressed by ζ (Schroeder 1962, Fisher 1964); the matrix elements of the O$_h$ component of V_L occur only on the main diagonal line of each matrix and are determined by the related O$_h$ strong-field configuration and expressed by $\Delta = 10D_q$; the pure C$_{3v}$ components of V_L, which are the only part we need to calculate, distribute within each Γ'(C$_{3v}^*$) block and are expressed by the one-electron matrix elements of V_L(C$_{3v}$) in the O$_h$ representation. Thus each of the matrices has a quasi-diagonal form composed of $S\Gamma$ blocks (for V_e), Γ' blocks (for V_{so}) and Γ' blocks (for the pure C$_{3v}$ part of V_L).

3. Digital results

We denote the single d-electron states by d_i:
$$d_i = \theta, \varepsilon, \xi, \eta, \zeta \qquad i = 1, 2, 3, 4, 5.$$
Then the non-vanishing matrix elements d_{ij} ($= \langle d_i | V_{C_{3v}} | d_j \rangle$) of the pure C$_{3v}$ crystal field are

$$d_{34} = d_{35} = d_{45} = a \qquad d_{24} = -d_{23} = b \qquad\qquad (1)$$

where a and b are reduced matrix elements.

The forms of the spatial parts of the d^4 (d^6) quintet states are exactly the same as that of the single d orbitals. Therefore when the spin–orbit coupling is neglected, the spin-allowed transition spectrum among the quintets is identical with the energy spectrum determined from the one-electron crystal-field matrix in the same approximation. The transitions among the quintets are shown in figure 1.

Two relations between the crystal-field parameters Δ, a and the observed spin-allowed transitions $\bar{\nu}_{min}$, $\bar{\nu}_{max}$ can be obtained:

$$\Delta = -(2\bar{\nu}_{max} + \bar{\nu}_{min}) \qquad a = -(\bar{\nu}_{max} - \bar{\nu}_{min}). \qquad\qquad (2)$$

Although the observed strong band at $23000\ \text{cm}^{-1}$ can be explained by a pairwise excitation transition $^5E \rightarrow {}^5T_2$ induced by the interchain exchange interaction associated with adjacent Cr^{2+} ions (McPherson *et al* 1972, Alcock *et al* 1976), we think that the broad strong band in the neighbourhood of the $6300\ \text{cm}^{-1}$ band should belong to a spin-allowed transition. Thus we take

$$\bar{\nu}_{min} = 6250\ \text{cm}^{-1}\ \text{(Cs)}$$

$$= 6710\ \text{cm}^{-1}\ \text{(Rb)}$$

$$\bar{\nu}_{max} = 11500\ \text{cm}^{-1}\ \text{(Cs)}$$

$$= 11730\ \text{cm}^{-1}\ \text{(Rb)}.$$

It is shown from the numerical analysis that the fine structures of the energy spectra in the region 16000–$25000\ \text{cm}^{-1}$ cannot be explained if $\bar{\nu}_{min}$ is reduced to zero, while the strong peak in the neighbourhood of the $6500\ \text{cm}^{-1}$ band can be assigned to spin-allowed absorption as is necessary and reasonable.

Once Δ and a are determined, we can use least-squares fitting to select the values of ξ, B, C, b for $CsCrCl_3$ and $RbCrCl_3$ respectively; then the transitions for $\Delta S = 0$ and $\Delta S = 1$ (there is some mixture between them) and the zero-field splitting of the ground state can be obtained. If vibronic coupling, the double d excitation and the splitting induced by spin–spin coupling are considered further, the calculated results will all be consistent with experiment (see tables 1 and 2).

In a strict trigonal crystal field there is no EPR in the ground state of Cr^{2+} (d^4). However, under a synthetic action of the interelectronic repulsion, the crystal field and the spin–orbit coupling, the ground state will be $A_1'(1)$. Although there is a mixture of configurations, the main composition is still just $t_2^3(^4A_2)e$ (here $e = \varepsilon$). The induced Jahn–Teller effect requires the complex ions to extend in the x–y plane. The related EPR g-factor of this ground state can be calculated using the formula of Griffith (1961): for $RbCrCl_3$ ($\Delta = 10056\ \text{cm}^{-1}$, $\xi = 180\ \text{cm}^{-1}$) we find

$$g_\parallel = 1.964 \qquad g_\perp = 1.991 \qquad g = 1.982$$

(Tazuke *et al* (1984) find $g = 1.988$) and for $CsCrCl_3$ ($\Delta = 9750\ \text{cm}^{-1}$, $\xi = 230\ \text{cm}^{-1}$) we find

$$g_\parallel = 1.953 \qquad g_\perp = 1.988 \qquad g = 1.976$$

(Tazuke *et al* (1984) find $g = 1.932$). This is in better agreement with experiment. The deviation is due to the fact that the configuration mixing used to calculate the g-factors is not complete.

However, as there is configuration mixing, it is rather difficult to determine the Jahn–Teller distortion. Even so, our result is still better than that of the Q_2 model of Tanaka *et al* (1986). Of course, the difference is a small one for the excited state.

4. Conclusion

In the present paper the complete $C_{3v}^*(d^4)$ strong-field matrices are built up in a block quasi-diagonal form by using the Griffith standard bases of the O_h^* double group. The absorption spectra and the ground-state zero-field splitting in $Cs(Rb)CrCl_3$ crystals are then calculated. The spin-allowed and spin-forbidden transitions, the vibronic coupling, the double d excitation induced by the strong interchain exchange interaction and the splitting induced by spin–spin coupling are all considered simultaneously in the spectrum analysis. It is shown from the good agreement between the theoretical results and the experimental findings that this scheme is reasonable.

The main points of this work are summarised below.

(*a*) There is a spin-allowed strong band in the neighbourhood of the 6500 cm⁻¹ band in addition to the transition for $\Delta S = 1$.

(*b*) The zero-field splitting values of the ground state calculated by us are 2.117–10.248 cm⁻¹ (Cs) and 1.885–6.456 cm⁻¹ (Rb). These values can be examined by the analysis of the EPR spectrum.

(*c*) We think that the 16 absorption peaks in the 15 800–19 000 cm⁻¹ region can by no means be explained by an O_h crystal field and spin–orbit coupling. In order to explain the complicated structure in this region of the spectrum vibronic coupling and energy splittings induced by the spin–spin interaction must also be considered in addition to the splitting induced by the C_{3v} crystal field.

(*d*) It is impossible to explain the strong bands in the neighbourhood of the 21 010 cm⁻¹ (Cs) and 21 277 cm⁻¹ (Rb) bands by means of single d-electron transitions. We attribute these bands to the double d electron simultaneous transitions for $\Delta S = 0$ (A_1' (5) (Cs) or A_1' (4) (Rb)) and $\Delta S = 1$ (α(Cs) or γ'(Rb)) induced by interchain exchange interaction between adjacent Cr^{2+} spins. Though the α or γ' belongs to the weak absorption for $\Delta S = 1$, the spectrum bands are close to the strong absorption at 11 500 cm⁻¹ (Cs) and 11 700 cm⁻¹ (Rb). Then, owing to the configuration mixing, the strong influence from the adjacent quintet state will be included in α and γ' and the probability of this double d absorption may increase. If the influence of the quintet on the triplet is small, this probability may decrease. However, these bands have not been explained by previous works.

(*e*) It is shown from our quantitative calculation that the strong band in the neighbourhood of 23 200 cm⁻¹ may be assigned to a double d excitation ($\Delta S = 0$) induced by interchain exchange coupling of adjacent Cr^{2+} ions. This conclusion is consistent with the quantitative explanation of Alcock *et al* (1976) and Mcpherson *et al* (1972).

(*f*) The calculated result for the *g*-factor is consistent with the observed one after considering the ground-state EPR induced by the Jahn–Teller effect of the Cr^{2+} ions.

Finally, the spin singlet has been ignored in this paper because of its very limited influence. Also, because the complete configuration admixture is considered in calculating absorption bands, polarisation absorption has been ignored. Then all of the transitions are possible and a quantitative analysis of oscillator strength will be very difficult. However, the method used in this paper is suitable for the complex ions of d^6 (C_{3v} or its isomorphic groups) where the signs of some parameters and the ground state will be different. Using this O_h^* point group representation of the strong-field scheme with a block quasi-diagonal form and the complete configuration interaction makes it very convenient to study the optical and magnetic properties of $d^N(G)$ complex ions.

Acknowledgment

Zhao Sang-bo et al

Table 2. (*a*) The spectrum analysis of $CsCrCl_3$ for $\Delta S = 1$.

C_{3v}^* Transition $A_1'(1) \rightarrow$	Calculated $\Delta S = 1$ Band (cm^{-1})	Observed (cm^{-1}) (Alcock *et al* 1976, Grama *et al* 1978)	O_h(calculated) (Mcpherson *et al* 1972)
E'	7150	7220	6570($^3T_1$)
A_1'	7679		
E'	8643		
A_2'	9293		
A_1'	9312(α)		
E'	9764		
E'	15863	15893	14830($^1T_2$)
A_2'	15924	16000(β)	15770(^1E)
$\beta + \bar{\nu}$		16090	15790(^3E)
E'	16218		
A_1'	16325		
A_2'	16350		
E'	16383	16434	
A_1'	16542	16608(γ)	16620($^2T_1$)
$\gamma + \bar{\nu}$		16708	
$\gamma + 2\bar{\nu}$		16801	16724(^3E)
E'	17045	16814(δ)	
$\delta + \bar{\nu}$		16915	
$\delta + 2\bar{\nu}$		17007	
A_1'	17411	17534	17290(^2T)
E'	17425		
A_2'	17621	17569	
A_1'	18144	18067	18298($^3A_2$)
A_2'	18335		
E'	18585	18755	18790($^3A_1$)
A_1'	18769	18772	18930($^3A_1$)
E'	19326		
E'	19983	19920	
E'	20468		
A_2'	20492		
$A_1'(5) + \alpha$	20970	21010(S)	21050($^1A_1$)
A_1'	22259		21600($^1A_1$)
E'	22327		
A_2'	22385	22420	23850($^1A_2$)
E'	23832		
A_1'	24209	24154	24030($^1T_2$)
E'	24617	24390	
E'	24855		
Parameters (cm^{-1})	$\Delta = 9750$ $a = 1750$ $b = 41$ $B = 765$ $C = 3162$ $\xi = 230$	$\bar{\nu} = 100$	$\Delta = 11450$ $B = 735$ $C = 3043$

Table 2. (*b*) The spectrum analysis of RbCrCl$_3$ for $\Delta S = 1$.

C$_{3v}^*$ Transition A$_1'$(1) →	Calculated $\Delta S = 1$ Band (cm^{-1})	Observed (cm^{-1}) (Alcock *et al* 1976, Grama *et al* 1978)	O$_h$(calculated) (Alcock *et al* 1976)
E$'$	6828		6574(^{3}T$_1$)
A$_1'$	7335		
E$'$	8260(α)		
A$_2'$	8880(β)		
A$_1'$	8940		
E$'$	9325(γ)		
A$_1'$(2) + α	15038	15060(vw?)	
E$'$(5) + β	15598	15418(vw?)	
E$'$	15828	15818	15862(^{3}T$_1$)
A$_2'$	15872	15886(ε)	
$\varepsilon + \bar{\nu}$	15936	15936	
A$_1'$(3) + γ	16103	16077	
E$'$	16149	16155	
A$_1'$	16228	16181	
A$_2'$	16301		
E$'$	16325	16515	16440(^{3}E)
A$_1'$	16505	16666	
Spin–spin splitting		16750	
Spin–spin splitting		16772	
Spin–spin splitting		16773(δ)	16724(^{3}E)
$\delta + \bar{\nu}$	16823	16829	
$\delta + 2\bar{\nu}$	16873	16871	
$\delta + 3\bar{\nu}$	16923	16906	
E$'$	16959	16964(ζ)	
$\zeta + \bar{\nu}$	17014	17021	
$\zeta + 2\bar{\nu}$	17064	17094	
A$_1'$	17325	17197	
E$'$	17328	17241	
A$_2'$	17519	17528	
A$_1'$	18017	17553	18298(^{3}T$_2$)
A$_2'$	18231	17794	
E$'$	18438	18622	18730(^{3}A$_1$)
A$_1'$	18658	18764	
E$'$	18981	18797	
E$'$	19850		20000(^{3}A$_1$)
E$'$	20304		20020(^{3}A$_2$)
E$'$	20316		
A$_1'$(4) + γ	21026	21050	
A$_1'$(5) + γ	21175	21277(strong)	
A$_1'$	22149		
A$_2'$	22220		
E$'$	22270	22676	
A$_1'$	23992	23095	23031(^{3}E)
E$'$	24346	24390	
Parameters (cm^{-1})	$\Delta = 10056$ $a = 1673$ $b = 41$ $B = 760$ $C = 3140$ $\xi = 180$	$\bar{\nu} = 50$	$\Delta = 11500$ $B = 800$ $C = 3200$

vw, very weak.

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