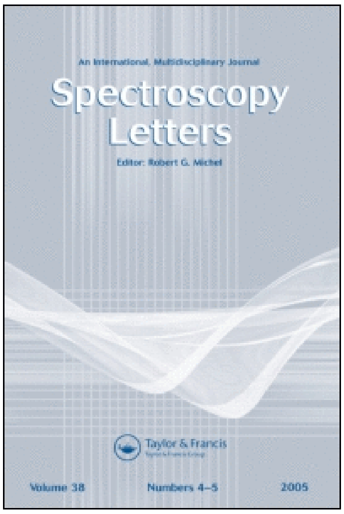

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ELECTRONIC ABSORPTION SPECTRUM OF Fe^{3+} DOPED IN AMMONIUM PERCHLORATE SINGLE CRYSTAL.

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ABSTRACT

Single crystals of Iron - doped ammonium perchlorate were grown at room temperature. The electronic absorption bands observed at room and liquid air temperatures have been assigned transitions from the ground $^6A_{1g}$ state to the excited $^4A_{1g}$, ^4E_g , $^4T_{1g}$ and $^4T_{2g}$ states. The crystal field parameters Dq = 870 cm^{-1}, B = 615 cm^{-1} and C = 4.2 B are found to give a good fit to the observed band positions.

INTRODUCTION

Ammonium perchlorate (NH_4ClO_4) belongs to the orthorhombic bipyramidal class (Wyckoff[1], Venkatesan[2]).

Though several studies such as neutron difraction (Smith et al[3]) Infrared (Waddington[4]) nuclear magnetic resonance (Inbers[5], Richards et al[7]) and heat capacity (Justice et al[7]) have been carried out on these Ammonium perchlorate crystals, no optical absorption work has so far been reported in literature. The authors therefore took up this investigation of work.

EXPERIMENTAL

Single crystals were grown from a solution of $FeCl_3 . 6H_2O - NH_4ClO_4$. In the present work, a crystal of thickness 2 mm containing 0.2 mole percent of iron was employed.

The optical absorption spectrum was recorded from λ 9000 A° to λ 3000 A° on a Hilger medium quartz spectrograph both at room and liquid air temperatures. The spectra were recorded in about 10 to 20 minutes on Kodak IN, Ilford Astra and Zenith plates.

Using microphotometric profiles recorded on a moll recording microphotometer, the wavelengths of the band maxima were measured against iron arc standard lines (Lakshman et al[8]).

THEORY

Iron has the electronic structure (A) $(3d)^6$ $(4\ s)^2$. The electronic configuration for Fe^{3+} is written as A $(3d)^5$. This configuration gives rise to ^{2}(S, P, D, F, G, H, I); ^{4}(P, D, F, G) and ^{6}S states of which ^{6}S lies lowest.

In a strong cubic crystalline field, the five valence electrons are distributed into the triply degenerate t_2 and doubly degenerate e orbitals. The ground state configuration for Fe^{3+} ion is then written as $t_2^3\ e^2$ which gives rise to the terms $^6A_1$, $^4A_1$, ^4E, $^4A_2$, $^4T_1$, $^4T_2$ and some other doublet states of which $^6A_1$ lies lowest.

Since $^6A_1$ is the only highest multiplicity term, all of the absorption bands result from spin-forbidden transitions. This fact is reflected in the very small oscillator strengths obtained for these bands.

RESULTS AND ANALYSIS

The microphotometric pnofiles of the bands recorded at liquid air temperature is shown in Fig. 1. The

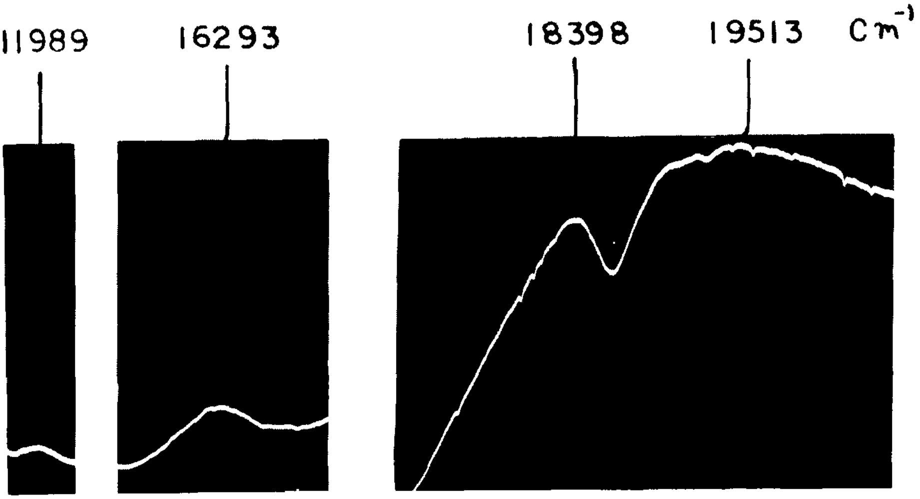

Fig. 1 Microphotometric Profiles of the Bands of Fe^{3+} in Ammoniumperclorate at 80°K

wave-lengths and wavenumbers of the bands obtained by the authors are presented in table 1 along with their assignments. From the nature and observed positions of the bands they have been assumed to belong to Fe^{3+} ion.

At room temperature, four bands have been recorded at 12002 cm^{-1}, 16388 cm^{-1}, 18398 cm^{-1} and 19513 cm^{-1}. The intensity of the spectrum is considerably increased when the crystal has been cooled to liquid air temperature.

Of the four bands observed, the band at 18398 cm^{-1} is found sharp and intense. Ligand field bands are sharp either when the energy expressions for the transitions are independent of Dq or when the number of t_2 electrons is the same in both the excited and ground

TABLE - I

Wavelength (λ), wave number (ν) and assignments for the bands of Fe^{3+} in ammonium perchlorate

Transitions from $^6A_{1g}$	Band Positions			
	300°K		80°K	
	$\lambda(A^o)$	$\nu(cm^{-1})$	$\lambda(A^o)$	$\nu(cm^{-1})$
$^4T_{1g}$	8330.0	12002	8339.0	11989
$^4T_{2g}$	6100.5	16388	6136.0	16293
$^4A_{1g}$	5434.0	18398	5434.0	18398
^4E_g	5123.5	19513	5123.5	19513

states (Ballhausen[9]). Therefore, the sharp band has to be attributed either to $^4A_1$ or ^4E states as they both have the same energy and their energy expressions are independent of Dq. Further no shift for such a band, according to Dunn[10] should be observed by cooling the crystal, which indeed has been observed to be so for this particular band.

Using Tanabe-Sugano[11] diagram given for d^5 configuration, the other bands at 12002 cm^{-1} and

16398 cm^{-1} are attributed to $^4T_{1g}$(G) and $^4T_{2g}$ (G) states respectively. On cooling the crystal, these bands showed a small red shift of (12002-11989) 13 cm^{-1} for the first and (16388 - 16293) 95 cm^{-1} for the second bands indicating a negative slope for the E verses Dq graph. Since only $^4T_{1g}$(G) and $^4T_{2g}$(G) levels have

TABLE - 2

The observed and calculated energies, Oscillator strengths and the assignments of the bands for Fe^{3+} in ammonium perchlorate.

(B = 615 cm^{-1} , C= 4.2 B and Dq = 870 cm^{-1})

Transitions from $^6A_{1g}$	Band Positions(cm^{-1})		f values	
	Observed at 80° K	Calculated	300° K	80° K
$^4T_{1g}$	11989	12290	--	6.20×10^{-5}
$^4T_{2g}$	16293	15833	2.28×10^{-5}	3.16×10^{-5}
$^4T_{1g}$	18398	19065	1.29×10^{-5}	2.36×10^{-5}
^4E_g	19513	19065	3.04×10^{-5}	4.6×10^{-5}

negative slopes, the assignments given above are confirmed.

Energy values are evaluated for $^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g}(G)$ and ^4E_g (G) states for different values of B, C and Dq by solving the energy expressions given by Lakshman et al[12]. Several sets of graphs have been drawn for different values of C between E and Dq. The inter-electronic repulsion parameter B and the crystal splitting factor Dq are then evaluated from the graph with C/B = 4.2 as shown in Fig. 2 to which the experi-

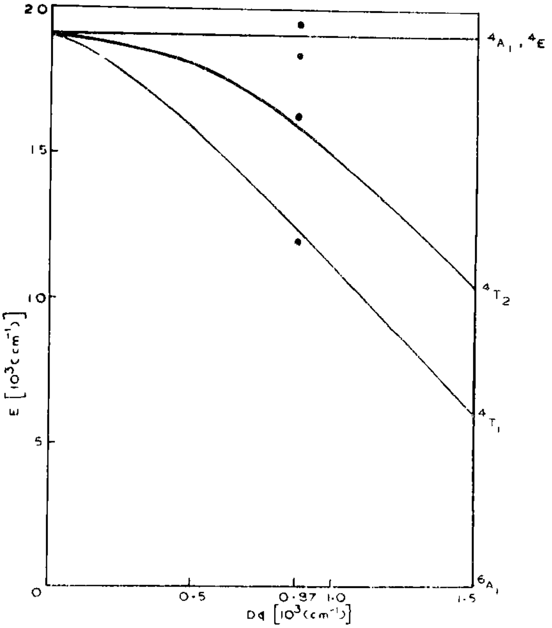

Fig. 2 Energy Level Diagram of Fe^{3+} in Ammonium Perchlorate in Cubic Environment Plotted as a Function of the Crystal Field Parameter Dq, with B=615 cm^{-1} and C=4.2B. The Solid Circles Show the Experimental Energies at 80°K.

mentally observed bands could very well be fitted. The calculated energy positions are presented in Table 2 along with the observed band maxima and their oscillator strengths.

DISCUSSION

As is seen from Table 3, energies of $^4A_{1g}(G)$ and $^4E_g(G)$ are different in the absence of configurational interaction (Lakshman et al[12]). It has been pointed out by Koide and Pryce[13] that this degeneracy can be lifted due to covalency in the crystal when the $^4A_{1g}$ state lies lowest than the ^4E_g state. The bands at 18398 cm^{-1} and 19513 cm^{-1} are therefore attributed to $^4A_{1g}$ and ^4E_g states respectively. It is interesting to note that these two bands did not show any shift on cooling the crystal indicating thereby that they are independent of Dq.

The B values for metal ions in crystals are smaller than for free ions and Jorgensen[14,15] attributes this decrease in B to covalent bonding in which metal *d* electrons occupy a greater volume encompassing metal and anion. This expansion of the electron clouds has been termed the Nephelauxetic effect. The ratio β(B/Bo), of the Racah parameter B for the ion in the complex to that of the free ion Bo is a measure of metal - anion

TABLE - 3

Energy expressions for some of the states of d^5 without configurational interaction

Transitions from $^6A_{1g}$	Energy expressions
$^4T_{1g}(G)$	$-10\ Dq + 10\ B + 6\ C$
$^4T_{2g}(G)$	$-10\ Dq + 18\ B + 6\ C$
$^4A_{1g}(G)$	$10\ Dq + 5\ C$
$^4E_g\ (G)$	$13\ B + 5\ C$
$^4T_2\ (D)$	$13\ B + 5\ C$
$^4E\ (D)$	$14\ B + 5\ C$

covalency. From a comparision of the values presented in Table 4, it is seen that the metal - anion covalency in the Ammonium perchlorate crystal is more or less the same as that found in Iron chloride or Iron doped Ammonium chloride crystals.

TABLE - 4

Values of B (cm^{-1}) and β for Fe^{3+} ion in some complexes

B_o (Free-ion) = 1085 cm^{-1} (Jorgensen[14])

Complex	B	$\beta = (B/B_o)$	Reference
$FeCl_4^-$	625	0.58	Jorgensen[14]
Fe^{3+} : NH_4Cl	645	0.59	Lakshman et al[16]
Fe^{3+} : NH_4ClO_4	615	0.57	Present work

The assignments for the bands are made assuming cubic crystalline field for the Fe^{3+} ion in the crystal. Since no splitting of the $^4T_{1g}$ or $^4T_{2g}$ bands could be observed in the present work, the site symmetry of the Fe^{3+} ion in the Ammonium perchlorate crystal could not be established with certainity. However, the broad nature of the ^4E_g band and the discrepancy in the experimental and theoretical values presented in Table 2 suggest that the Fe^{3+} ion is not entirely subjected to a cubic crystalline field but may also be under the influence of a lower symmetry field.

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