

Physics

OPTICAL ABSORPTION SPECTRUM OF  $\text{Fe}^{3+}$  IN ORTHOCLASE FELDSPAR

B. J. REDDY and K. B. N. SARMA

*Spectroscopic Laboratories, Department of Physics, S. V. University, Tirupati-517 502*

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The ion responsible for the bands in feldspar has been identified for the first time from spectrochemical analysis and optical absorption studies, as  $\text{Fe}^{3+}$ . Four bands have been observed at 16150, 17390, 19230 and 22220  $\text{cm}^{-1}$  in the visible region and three other bands at 37040, 45000 and 47600  $\text{cm}^{-1}$  in ultraviolet region. From the energy values of band positions, the former four bands and the latter three bands are assigned to spin-forbidden transitions and charge transfer spectra respectively, for  $\text{Fe}^{3+}$ . The crystal field parameters have been derived from the observed spectrum of feldspar as  $B = 710 \text{ cm}^{-1}$  and  $Dq = 780 \text{ cm}^{-1}$

INTRODUCTION

MOST of the silicates contain first group transition metals, and give rise to absorption bands in ultraviolet and visible regions (Manning, 1967; and Lakshman *et al.*, 1972) The authors proposed to study the absorption spectrum of one of such silicates, namely feldspar. Webster (1975) reported that feldspar exhibits broad and diffuse bands due to iron at 4480 Å, 4200 Å and 3750 Å. But no transitions are assigned to a definite ion. Therefore, the authors took up the present work, as there is no detailed analysis of the bands of feldspar reported in literature.

Feldspars are silicates of aluminium with the metals potassium, sodium and calcium. The chemical composition of orthoclase is  $\text{KAlSi}_3\text{O}_8$ . Each  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  is surrounded in a nearly ideal tetrahedral co-ordination by four  $\text{O}^{2-}$ . Thus each  $\text{O}^{2-}$  belongs to two neighbouring  $\text{SiO}_4$  or  $\text{AlO}_4$  tetrahedrons. Considering the  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$  alone, they form a three dimensional net-work (Encydo, 1971).

The visible portion of the absorption spectrum displays the features due to spin forbidden transitions of nearly octahedrally co-ordinated  $\text{Fe}^{3+}$ . The observed spectrum of feldspar in the UV and visible regions can be attributed to the impurity  $\text{Fe}^{3+}$  ions partially replacing aluminium. The crystal field exhibiting the spectrum could be assigned as approximate octahedral site symmetry. The embedded  $\text{Fe}^{3+}$  ions with close neighbours of  $\text{O}_2^-$  ligands, have a nearly octahedral formation.

EXPERIMENTAL

A brownish red coloured orthoclase feldspar ( $\text{KAlSi}_3\text{O}_8$ ) was collected from Karnataka State, India. As the sample possesses high opacity, its absorption spectrum could not be recorded even for a thin section. Since similar features of absorption can be exhibited by a sample either in crystal or mull form (Lakshman & Reddy, 1973), the absorption spectrum of feldspar in the mull form was recorded on Unicam SP700 Spectrophotometer, I.I.Sc., Bangalore. No bands were recorded for the sample in the near infrared region.

TABLE I

*Estimation of first transition metals present in orthoclase feldspar*

Element	Amount (ppm)
Titanium	25
Vanadium	18
Chromium	5
Manganese	2
Iron	2500
Copper	50

Spectrochemical analysis was carried out for detection and estimation of first group transition metals present in the sample, the details of which would be reported elsewhere. Only one transition element, namely iron was found to be present in higher concentration (2500 ppm) compared to other transition elements as given in Table I. So the present sample belongs to one of the iron rich potassium feldspars.

## THEORY

Iron has the electronic structure A(3d)<sup>6</sup> 4s<sup>2</sup>. For Fe<sup>3+</sup>, the electron configuration is written as A(3d)<sup>5</sup>. The electronic ground state of Fe<sup>3+</sup>, therefore, is <sup>6</sup>S. In octahedrally co-ordinated Fe<sup>3+</sup> complex, the lowest configuration is written as *t*<sub>2g</sub><sup>3</sup> *e*<sub>g</sub><sup>2</sup> which gives rise to <sup>6</sup>A<sub>1</sub> as the ground state. Since this is the only sextet level present, all the absorption bands result from spin-forbidden transitions.

## RESULTS AND ANALYSIS

The bands recorded on Unicam SP700 Spectrophotometer are shown in Fig. 1. Wavelengths, wavenumbers and assignment data for the bands of Fe<sup>3+</sup> in feldspar

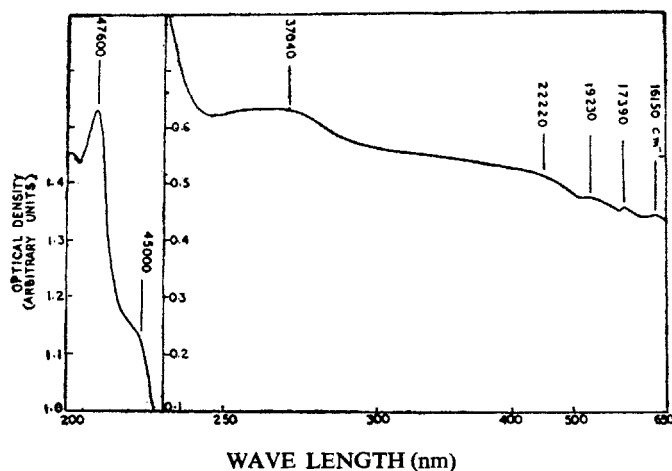


FIG. 1. Trace of the Spectrophotometric Record of the Bands due to Fe<sup>3+</sup> in Feldspar (Mull Form) recorded on Unicam SP 700 at 300 °K.

TABLE II

*Wavelengths, wavenumbers and assignments for the bands of Fe<sup>3+</sup> in feldspar at 300 °K*

Wavelength $\lambda$ (Å)	Band position in wavenumber $\nu$ (cm <sup>-1</sup> )	Assignment with respect to the ground state <sup>6</sup> A <sub>1</sub>
6200	16150	<sup>4</sup> T <sub>1</sub> (G)
5750	17390	<sup>4</sup> T <sub>2</sub> (G)
5200	19230	
4500	22220	<sup>4</sup> A <sub>1</sub> , <sup>4</sup> E(G)
2700	37040 (4.6 eV)	Charge transfer bands
2220	45000 (5.6 eV)	
2100	47000 (5.8 eV)	

are given in Table II. In view of higher concentration of iron in the sample, the bands are to be attributed to iron ion. As discussed earlier the aluminium ion is replaced by iron ion, since the ionic radius of Fe<sup>3+</sup> (0.64Å) being of the order of ionic radius of Al (0.51Å), it might be possible for Fe<sup>3+</sup> ion to replace Al<sup>3+</sup> ion (Brian Mason, 1966 ; and Kondratyev, 1967). Substitution of Fe<sup>3+</sup> for Al<sup>3+</sup> might be favoured by identical valencies. Faust (1936) also established the replacement of Al by Fe<sup>3+</sup> in potassium feldspars. Therefore, the analysis is carried out with the assumption that the bands are due to Fe<sup>3+</sup> ion.

The absorption spectrum of Fe<sup>3+</sup> in feldspar consists of four main bands located at 16150 cm<sup>-1</sup>, 17390 cm<sup>-1</sup>, 19230 cm<sup>-1</sup> and 22220 cm<sup>-1</sup>. Of these bands, the band at 22220 cm<sup>-1</sup> is strong and the other three bands are somewhat sharp. For analysis of these bands, the energy matrices of *d*<sup>5</sup> configuration were solved on IBM 370 computer at I.I.T., Madras and Tanabe-Sugano diagrams were drawn for different ratios of *C/B*. The best fit of the observed bands was found to be at *Dq/B* = 1.1 for the ratio *C/B*=4.25. The values of *Dq* and *B* were found to be 780 cm<sup>-1</sup> and 710 cm<sup>-1</sup> respectively. So, from this diagram (Fig. 2), the band at 16150 cm<sup>-1</sup> was assigned to <sup>4</sup>T<sub>1</sub> (G) state and the bands at 17390 cm<sup>-1</sup> and 19230 cm<sup>-1</sup> were

TABLE III

*Observed and calculated energies and assignments of the bands for Fe<sup>3+</sup> in feldspar (Dq = 780 cm<sup>-1</sup>, B = 710 cm<sup>-1</sup>, and C = 3020 cm<sup>-1</sup>)*

Transition from <sup>6</sup> A <sub>1</sub> (S)	Band positions (cm <sup>-1</sup> )	
	Observed	Calculated (from graphs)
<sup>4</sup> T <sub>1</sub> (G)	16150	16030
<sup>4</sup> T <sub>2</sub> (G)	17390	19880
	19230	
<sup>4</sup> A <sub>1</sub> , <sup>4</sup> E (G)	22220	22190

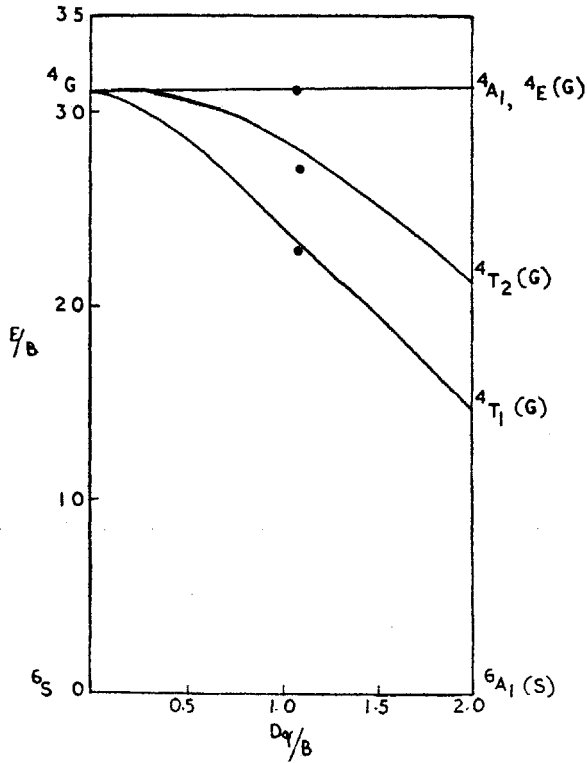


FIG. 2. Energy Level Diagram of Fe<sup>3+</sup> in cubic environment. Plotted as a function of the crystal field parameter  $Dq$  with  $B=710\text{ cm}^{-1}$  and  $C=4.25 B$ . The solid circles show the experimental energies at 300 °K.

assigned to  ${}^4T_2(G)$  state and the other band at  $22220\text{ cm}^{-1}$  is attributed to  ${}^4A_1, {}^4E(G)$  state. The observed and calculated energies and the assignment of the bands due to Fe<sup>3+</sup> ion in feldspar are presented in Table III.

The bands observed at  $37040\text{ cm}^{-1}$ ,  $45000\text{ cm}^{-1}$  and  $47000\text{ cm}^{-1}$  might be due to charge transfer. The energies of the bands expressed in electron volts are 4.6eV, 5.6eV and 5.8eV. These bands might be due to charge transfer spectra of Fe<sup>3+</sup> (Robert *et al.*, 1974).

#### DISCUSSION

The absorption bands of orthoclase feldspar are attributed for the first time to Fe<sup>3+</sup> ion. The assignment of Fe<sup>3+</sup> bands is made assuming nearly octahedral symmetry. Fe<sup>3+</sup> bands are due to spin-forbidden transitions. The chemical analyses of orthoclase feldspars reported earlier (given in Table IV) (Maxwell *et al.*, 1965; and Smith, 1974) revealed that the presence of ferrous iron is almost negligible. It may be concluded that the ferrous iron reported in the case of iron rich potassium feldspars is either nil or small (Deer *et al.*, 1962). The Fe<sup>2+</sup> ion should give rise to bands in the near infrared region. But no bands were detected in the near infrared

TABLE IV  
Analyses of orthoclase feldspar of different localities

Component	Canadian Sample (Maxwell, 1965)	Indian Sample (Tamil Nadu) (Smith, 1974)
SiO <sub>2</sub>	63.46	63.01
Al <sub>2</sub> O <sub>3</sub>	18.78	19.73
Fe <sub>2</sub> O <sub>3</sub> *	0.39	0.62
FeO	—	—
MgO	0.22	0.19
BaO	—	0.50
CaO	1.28	0.26
Na <sub>2</sub> O	2.17	1.51
K <sub>2</sub> O	13.92	14.53

\*Fe content in the above samples are 2700 ppm and 4340 ppm respectively.

region for the present sample. Therefore, the assignment of feldspar bands to Fe<sup>3+</sup> ion is justified.

The splitting of the band at 19230 cm<sup>-1</sup> (component 17390 cm<sup>-1</sup>) suggests that Fe<sup>3+</sup> ion is not entirely subjected to a cubic field, but may also be under the influence of trigonal or tetragonal field.

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