

MOSSBAUER, ESR AND OPTICAL SPECTRA OF HUMITE MINERAL

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Mossbauer, ESR and optical spectra of humite were studied for the first time. From the supplementary measurements of Mossbauer and ESR data, the five absorption bands observed at 15240, 18350, 20745, 25575 and 28570 cm^{-1} are attributed to Fe^{3+} ion in a slightly distorted octahedral site. The crystal field parameters which give a good fit for the observed band positions are $B = 690 \text{ cm}^{-1}$; $C = 2769 \text{ cm}^{-1}$ and $Dq = 760 \text{ cm}^{-1}$. The two bands observed in the near infrared region are assigned to Fe^{2+} ion in a more distorted octahedral site.

Key words: Optical absorption, Humite mineral crystal field parameters.

Introduction

Most of the silicate minerals contain first group transition metals as impurities and their optical spectra have been used to determine the local symmetry of an-ionic environment around the cation [1-5]. Optical absorption and mossbauer spectra of many silicates bearing ferrous and ferric ions have been reported elsewhere [6-11], but no attempt has been made so far with humite. The authors therefore decided to investigate the ionic nature of iron in humite by utilizing mossbauer, ESR and optical absorption techniques.

Humites are structurally analogous to olivine and have restricted occurrence. In this mineral $3\text{Mg}_2\text{SiO}_4\text{Mg}(\text{OH},\text{F})_2$ there are four Mg octahedra and two Si-O tetrahedra. Fe, Mn, Ti, Ca and Zn may replace Mg. Ferrous iron replaces Mg in the $\text{Mg}(\text{OH},\text{F})\text{O}$ region of the structure [12,13] with five O and one (OH,F). Structural analysis of humite by Ribbe *et al.* [12] reveals that ferrous iron is ordered into more distorted octahedra with six oxygen ligands.

Theory. The ground state electron configuration of Fe^{3+} ion is $\text{A}(3d)^5$, where A stands for closed argon shell. In octahedral field, these five valence d electrons are distributed in t_{2g} and e_g orbitals with three in the former and two in the latter. Therefore the ground state configuration is written as $t_{2g}^3 e_g^2$. This gives rise to the electronic states ${}^6A_{1g}$, ${}^4A_{1g}$, 4E_g , ${}^4T_{1g}$ and ${}^4T_{2g}$ and a number of doublet states of which ${}^6A_{1g}$ lies lowest as per Hund's rule. The other excited electron configurations like $t_{2g}^4 e_g$, $t_{2g}^2 e_g^3$ and $t_{2g} e_g^4$ gives rise to several quartet and doublet states. Thus all the absorption bands of Fe^{3+} results from the spin-forbidden transitions and they are expected to be weak.

The ground state configuration for Fe^{2+} ion in an octahedral field is written as $t_{2g}^4 e_g^2$. This gives rise to electronic states ${}^5T_{2g}$, 3E_g , ${}^3T_{1g}$, ${}^3T_{2g}$ and some triplet and singlet states of which ${}^5T_{2g}$ forms the ground state. The other configurations gives rise to several triplet and singlet states and one quintet state 5E_g . Thus ${}^5T_{2g} \rightarrow {}^5E_g$ transition alone is expected to be strong and other spin-forbidden transitions are weak.

From the S-ground state there exists a zero-field splitting even in a cubic field and so ESR spectrum of Fe^{3+} usually does not show any fine structure.

The EPR spectrum of a given Mn^{2+} centre should consists of five fine structure transitions ($\Delta m \pm 1$). The nuclear spin of ${}^{55}\text{Mn}$ is $5/2$. Therefore the total hyperfine structure consists of six lines ($\Delta m = 0$) for each fine structure transition.

Mn^{2+} is more sensitive than Fe^{3+} ion for ESR studies and the characteristic six line spectrum of Mn^{2+} appears in the ESR spectrum eventhough Mn^{2+} is present in traces.

Experimental

The reddish brown humite mineral sample collected from Malagasy Republic was kindly supplied by the Geological Survey of Canada. The optical absorption spectrum of the powdered sample was recorded on Carry 17D spectrophotometer in the region 200-2000 nm and ESR spectra at room and low temperatures on JEOL X-band spectrometer. Mossbauer measurements of the samples at room temperature were made with a constant acceleration electromechanical drive and multichannel analyser system, with Co-57 in rhodium matrix as the source. Spectrochemical analysis was employed as described by Reddy *et al.* [7] for the detection and determination of transition metals that are present in humite mineral. From this study the presence of transition metals were estimated in the mineral as $\text{Fe} = 1000$; $\text{Mn} = 20$ and $\text{Ti} = 100$ ppm. Therefore optical spectrum of humite is attributed to iron which is present in higher concentration.

Results and Discussion

Mossbauer studies. The Mossbauer spectrum of humite consists of two symmetrically disposed quadrupole doublets superimposed as shown in Fig. 1. Several workers have observed similar doublets in minerals [14,15] and assigned them to Fe^{3+} and Fe^{2+} species. From the Mossbauer spectrum of the sample of the chemical shifts are found to be 0.46 and 1.0 mm/s for the Fe^{3+} and Fe^{2+} species respectively and

quadrupole splittings are found to be 1.22 and 2.42 mm/s for the two species respectively. A comparison of these values is made with the mossbauer parameters of other iron silicates of known crystal structures given by Boncroft *et al.* [16] and are presented in Table 1. It is seen from the Table that the Fe^{3+} ion is cited in a less distorted octahedron and Fe^{2+} in a more distorted octahedron.

ESR measurements. The first and second derivatives ESR spectra of humite at 300 K and 120 K have been studied and Fig. 2 shows the first derivative ESR spectrum of humite at 120 K (9.214 GHz and 1 mw). The spectrum has close resemblance with that of MgO bearing Mn and Fe obtained by Auzins *et al.* [17], and the values of A for Fe^{3+} and Mn^{2+} were reported as 11.4 and 70.8 respectively. At 120 K only the ESR spectrum of humite gave $1/2 \leftrightarrow -1/2$ transition of Fe^{3+} at its turning points ($g = 2.008 \pm 0.005$). The linewidth of Fe^{3+} showed a marked temperature dependence. At 300 K it is almost too broad for detection and at 120 K it is nearly $11 \times 10^{-4} \text{ cm}^{-1}$. This value is similar to that obtained for Fe^{3+} in oxide systems [18]. The six line transition corresponds to $1/2 \leftrightarrow -1/2$ transition of Mn^{2+} ($\Delta M = \pm 1$ and $\Delta m = 0$). Forbidden hyperfine lines ($\Delta m = \pm 1$, labelled f) also appear as intermediate pairs [19]. The evaluated parameters are $g = 2.005 \pm 0.005$ and $A (80 \pm 2) \times 10^{-4} \text{ cm}^{-1}$ and are found to be independent of temperature within the experimental error. The area under any transition is very nearly the same and this suggests isotropic nature of g.

Optical absorption studies. The optical absorption spectrum of nujol mull of humite sample in the UV-VIS regions at 300 K is shown in Fig. 3. It has features similar to those of Fe^{3+} in other silicate minerals as observed by Lehmann *et al.* [20] and Manning [21]. It consists of four bands in the visible and two bands in the UV region. The bands

at 15240 and 18350 cm^{-1} are broad and the bands at 20745 and 25575 cm^{-1} are rather sharp. The two broad bands are assigned to ${}^4\text{T}_{1g}(\text{G})$ and ${}^4\text{T}_{2g}(\text{G})$ states respectively and two sharp bands to ${}^4\text{A}_{1g}$, ${}^4\text{E}_g(\text{G})$ and ${}^4\text{E}_g(\text{D})$ states respectively. With the

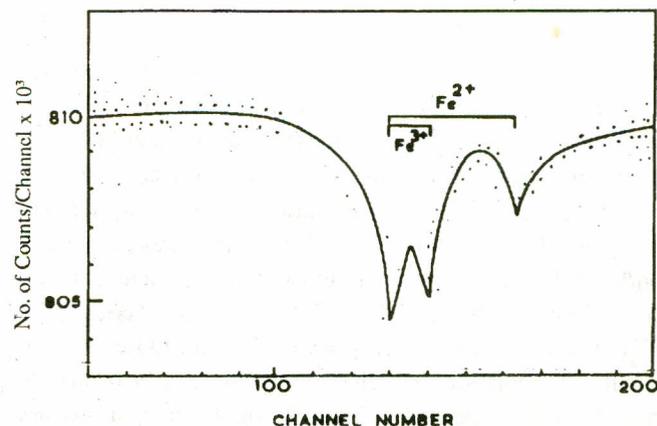


Fig. 1. Mossbauer spectrum of humite at 300 K.

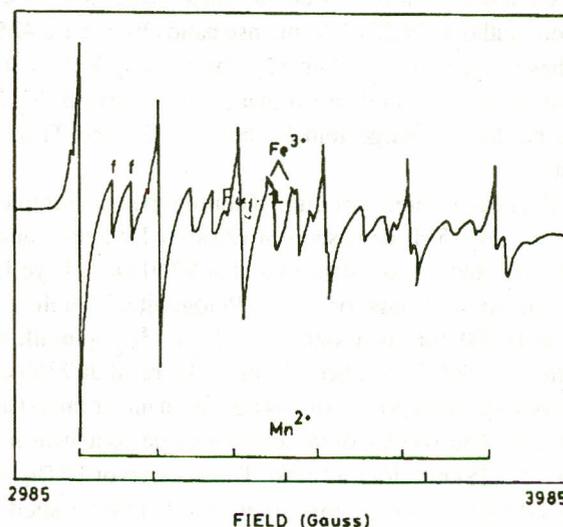


Fig. 2. ESR spectrum of humite at 120 K.

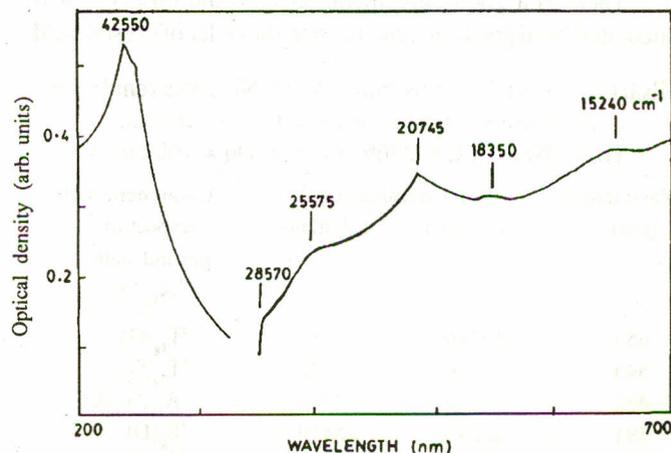


Fig. 3. Optical absorption spectrum of Fe^{3+} in humite at 300 K.

TABLE 1. MOSSBAUER PARAMETERS FOR IRON SILICATES OF KNOWN CRYSTAL STRUCTURES (16).

Mineral	Type of iron	Chemical shift mm/s	Quadrupole splitting mm/s	Site symmetry
Andradite garnet	Fe^{3+}	0.50	0.58	Octahedron
Epidote	Fe^{3+}	0.43	2.01	Irregular octahedron
Olivine	Fe^{2+}	1.25	2.9	Octahedron
Orthopyroxene	Fe^{2+}	1.23	1.91	Distorted octahedron
Almandine garnet	Fe^{2+}	1.40	3.55	Distorted cube
Humite (Present work)	Fe^{3+}	0.46	1.22	Distorted octahedron
	Fe^{2+}	1.00	2.42	Distorted octahedron

observed band positions, Racah parameters B and C are evaluated with the following Tanabe-Sugano equations [22].

$$v_1 = E(^4A_{1g}, ^4E_g(G)) - E(^6A_{1g}(S)) = 10B + 5C \dots\dots (1)$$

$$v_2 = E(^4E_g(D)) - E(^6A_{1g}(S)) = 17B + 5C \dots\dots\dots (2)$$

and are found to be $B = 690$ and $C = 2769 \text{ cm}^{-1}$ respectively. The energy matrices given by Tanabe and Sugano [23] for d^5 configuration have been diagonalised and solved on IBM 370 computer. Energy level diagram drawn between E/B and Dq/B for the ratio $C/B = 4.0$ with various values of Dq is shown in Fig. 4. The best fit of the experimental values is found at $Dq/B = 1.1$. Thus the crystal field splitting parameter is found to be 760 cm^{-1} . The band at 28570 cm^{-1} could be assigned to $^4T_{1g}(P)$ state from the energy level diagram. Observed and calculated energies along with the assignment of the bands due to Fe^{3+} ion are presented in Table 2. The band positions and crystal field parameters for Fe^{3+} ion in humite are similar to those obtained in various oxide host materials as observed by previous authors [24,25]. The intense band observed at 42550 cm^{-1} has the same order of energy observed by Robert *et al.* [26] in the case of Fe^{3+} in synthetic acmite (Mg_2SiO_4) and might be due to charge transfer between Fe and Ti in the sample.

The near infrared spectrum of humite (powder sample) is shown in Fig. 5. It consists of a broad and intense band at 10990 cm^{-1} and a less intense band at 9260 cm^{-1} . Faye [27] observed similar bands for Fe^{2+} in Phlogopite. Therefore the band at 10990 cm^{-1} is assigned to $^5T_{2g} \leftrightarrow ^5E_g$ spin-allowed transition of Fe^{2+} in octahedral field. The band at 9260 cm^{-1} might be a split component of this transition under Jahn-Teller effect [28]. The average of these two energies is a measure of $10Dq$ (-10125 cm^{-1}) for Fe^{2+} [29]. The position of $10Dq$ band observed for Fe^{2+} in the sample indicates that Fe^{2+} is sited in a more distorted octahedron [27].

There is a good agreement between the observed and calculated band positions, and further, the order of crystal field

TABLE 2. WAVE LENGTHS (nm), WAVE NUMBERS (cm^{-1}) AND ASSIGNMENT OF THE BANDS OF Fe^{3+} IN HUMITE. ($B = 690 \text{ cm}^{-1}$; $C = 2769 \text{ cm}^{-1}$ and $Dq = 760 \text{ cm}^{-1}$)

Wave length (nm)	Wave number (cm^{-1})		Assignment with respect to ground state $^6A_{1g}(S)$
	observed	calculated	
655	15240	15035	$^4T_{1g}(G)$
545	18350	18492	$^4T_{2g}(G)$
482	20745	20700	$^4A_{1g}, ^4E_g(G)$
391	25575	25530	$^4E_g(D)$
350	28570	28732	$^4T_{1g}(P)$

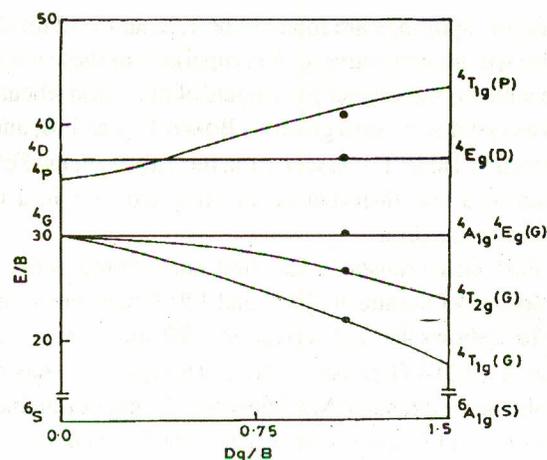


Fig. 4. Energy level diagram of Fe^{3+} in octahedral field plotted as a function of crystal field parameter Dq with $B = 690 \text{ cm}^{-1}$ and $C = 4.0 B$. The solid circles show experimental energies at 300 K.

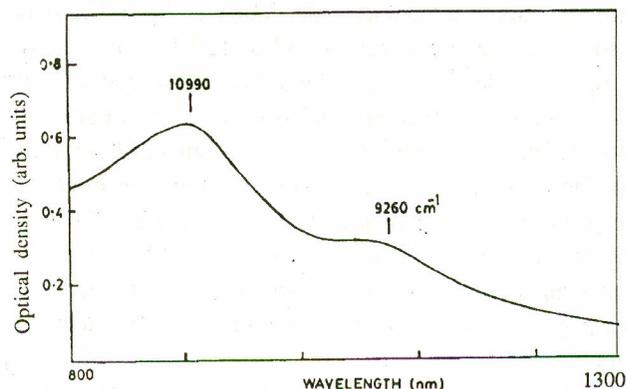


Fig. 5. Optical absorption spectrum of Fe^{2+} in humite at 300 K.

parameters in humite sample confirm the Fe^{3+} site [30,31]. The values of g and A obtained for Mn^{2+} and Fe^{3+} ions in humite agree well with the data given for octahedral sites for $3d^5$ ions [32,33]. From the supplementary measurements of Mossbauer and ESR studies, the optical absorption spectrum of humite in visible region could successfully be assigned to Fe^{3+} ion in a slightly distorted octahedral site, whereas the two bands in the near infrared spectrum could be assigned to Fe^{2+} ion in a more distorted octahedral site.

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