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Absorption and luminescence of Fe^{3+} in single-crystal orthoclase

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ABSTRACT

Polarized optical absorption spectra and laser-excited luminescence spectra have been measured on single-crystal Fe-rich orthoclase. The absorption spectrum consists of a series of sharp, weak bands that can be assigned to spin-forbidden crystal-field transitions of Fe^{3+} substituted on the tetrahedral Al^{3+} site of the feldspar structure. A broad-band luminescence in the deep-red region is the Stokes-shifted $^4T_1 \rightarrow {}^6A_1$ transition of tetrahedral Fe^{3+} and confirms the assignments of the absorption spectrum. The temperature dependence of the luminescence intensity can be accounted for by a phonon-assisted nonradiative decay process.

INTRODUCTION

Fe^{3+} enters the feldspar structure by substituting for Al^{3+} on the tetrahedral sites. Of the various feldspars examined, the Fe-rich, gem-quality orthoclases from Madagascar (Coombs, 1954) provide excellent specimens for detailed examination of the optical spectrum of Fe^{3+}.

Fe^{3+} has the d^5 electron configuration, and all crystal-field transitions from the $^6A_1$ ground state are spin-forbidden. The crystal-field spectrum of Fe^{3+} is weak and is easily obscured by intervalence electron-transfer absorption if small amounts of Fe^{2+} are present. Spectra of Fe^{3+} have been observed in garnets, in jade, and other minerals as well as in the feldspars (Bell et al., 1975; Burns and Vaughan, 1975). Unpolarized spectra of Fe^{3+} in the Madagascar feldspars were reported by Faye (1969) and reinterpreted by Manning (1970). The Fe^{3+} spectrum in orthoclase is generally similar to the spectra of plagioclases (Bell and Mao, 1973) as revealed by the detailed examination of feldspar optical spectra by Hofmeister and Rossman (1984).

Many feldspars exhibit a characteristic red luminescence, particularly under electron-beam excitation, which has been ascribed to the $^4T_1 \rightarrow {}^6A_1$ transition in the Fe^{3+} (Smith, 1974; Geake and Walker, 1975). The same transition is responsible for the strongly luminescent character of the isoelectronic Mn^{2+} ion. The red luminescence appears in the feldspar grains in granites (Blair and Edgington, 1970) and has been found in lunar plagioclases (Telfer and Walker, 1975). Indeed it has been argued that the reddish glow seen on the Moon during the early stages of a total eclipse is due to feldspar luminescence excited by the solar wind.

The present paper gives detailed measurements on both absorption and luminescence spectra of the Fe-rich Madagascar feldspars and re-examines the assignment and interpretations that have been made.

SOURCE OF SAMPLES AND EXPERIMENTAL METHODS

Single crystals of feldspar were obtained from various sources (Table 1). All were transparent with no evidence for exsolved phases. The color varied from nearly colorless to yellow and was clearly related to the Fe content. Emission spectrographic analyses gave the minor trace-element content. An analysis for Fe by direct titration and by atomic absorption is given in Table 1. Fe^{2+} was below the threshold for detection by the methods used.

Absorption spectra were measured on a Cary model 14 spectrophotometer. The crystals were oriented by back-reflection Laue methods, and slices were cut perpendicular to the indicatrix axes. The polarization dependence of the spectra was determined by placing a pair of Glan prisms in both the sample and the reference beam of the spectrophotometer. Spectra at 78 K were obtained using a liquid N_2 dewar that fitted into the spectrophotometer beam.

The luminescence of the feldspars was excited using the 476.5- and 488-nm lines of an Ar ion laser. A Spex model 1400 Raman spectrometer with red-sensitive RCA C31034 photomultiplier was used to measure the luminescence spectra. Because the laser beam is intrinsically polarized, it was possible to determine the polarization dependence of the Fe^{3+} emission with respect to the indicatrix axes of the feldspar crystals. An Air-Products Helitran system was used to determine the temperature dependence of luminescence spectra from room temperature to liquid N temperature.

RESULTS

The polarized absorption spectrum of sample 1392 is shown in Figure 1. The spectrum consists of a strong sharp band near 26 000 cm^{-1}, two medium-intensity bands near 24 000 cm^{-1}, and several broader weak bands in the range 20 000 to 16 000 cm^{-1}. Wavenumbers for these bands from the unpolarized spectra measured on all specimens are tabulated (Table 2). The bands are arbitrarily labeled ν_1 to ν_6 in order of decreasing wavenumber for convenience in discussion. All bands appear in all polarization directions. There are small changes in intensity, but this effect

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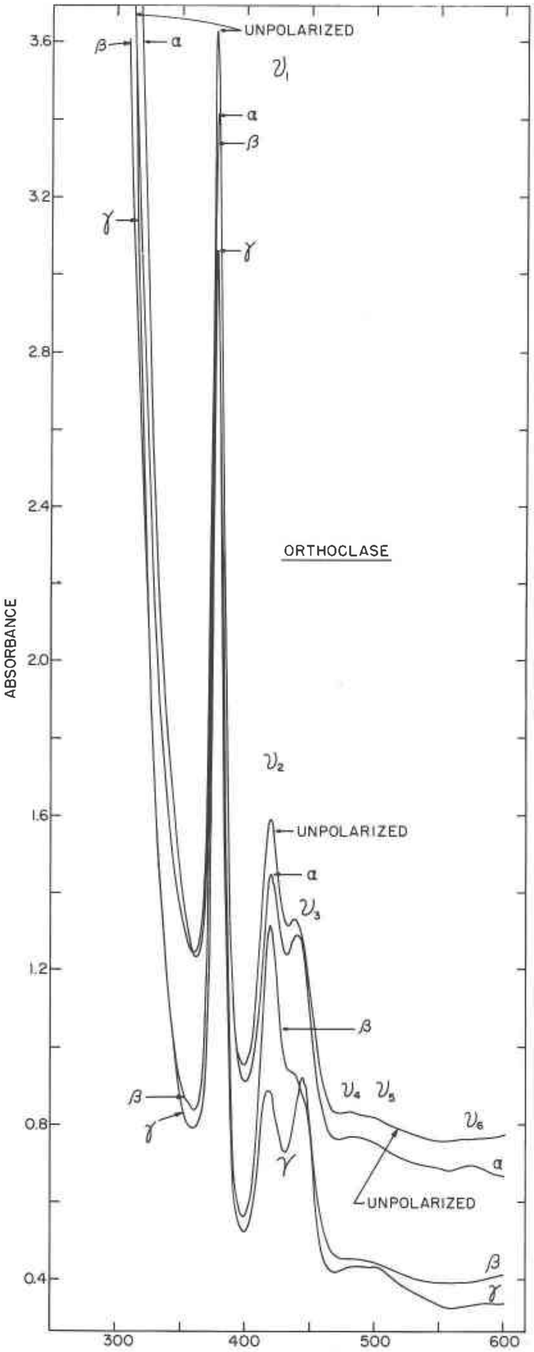

Fig. 1. Electronic absorption spectra for orthoclase specimen 1392. The absorbance scale is for the γ spectrum; others have been displaced for clarity.

is most pronounced in ν_3, which appears as a strong component in the γ spectrum but only as a shoulder in the β spectrum.

Table 1. Sources and analyses of Fe-containing orthoclase

Sample no.	Source in Madagascar	Fe_2O_3* wt%	Minor elements**	Trace elements†
1391	Ampandrandava	0.42	Ba, Ti	Ca, Be, Sr
1392	Itrongay	1.58	Ba, Ti, Be	Ca, Sr, Mn
1393	Betroka	0.41	Ba, Ti	Ca, Be, Sr
106825‡	Itrongay	1.95	Ba, Ti, Be	Ca, Sr, Mn

* Total Fe by atomic absorption. FeO by direct titration was less than 0.1 wt% in all specimens.

** Concentration range: 0.02 to 2.0 wt%.

† Concentration range: <0.02 wt%.

‡ U.S. National Museum specimen number.

Following the usual conventions, the optical absorption spectra were measured with electric vector parallel to each of the three indicatrix axes. However, in an absorbing crystal, the refractive index is a complex quantity

$$N^* = n + ik. \tag{1}$$

The indicatrix is a symmetric second-rank tensor with axis orientation determined by the maximum and minimum values of the real refractive index, n. The absorption coefficient α is related to k, the imaginary part of the refractive index, also called the extinction coefficient:

$$\alpha = 4\pi\nu k. \tag{2}$$

The extinction coefficient is also a symmetric second-rank tensor, but in the absence of symmetry constraints in the triclinic orthoclase structure, the principal absorption axes are not required to be parallel to the indicatrix axes. See Dowty (1978) for further commentary on this point.

Unpolarized spectra of specimen 106825 taken at 78 K are shown in Figure 2. There are some small changes in band intensity: ν_1, ν_2, and ν_3 increase intensity with decreasing temperature, while the others decrease. ν_3 splits into a definite doublet at low temperature. The weak bands ν_4, ν_5, and ν_6 are better defined in the spectrum of specimen 106825, making a more convincing argument that these bands are indeed part of the Fe^{3+} spectrum.

The variation in the absorption of ν_1 with Fe concentration (Fig. 3) gives a molar extinction coefficient of 3.7 $L \cdot mol^{-1} \cdot cm^{-1}$. This value is comparable to spin-allowed transitions in octahedral fields. It appears that the increase in intensity from the tetrahedral field is just about cancelled by the spin-selection rule. All other bands are proportionately weaker. Fe is magnetically dilute in these feldspar structures, and the enhancement of absorption due to magnetically coupled Fe^{3+}-Fe^{3+} pairs (Sherman, 1985) does not occur.

Under laser excitation there was a strong red luminescence from all specimens. The unpolarized spectrum (Fig. 4) consists of a single broad band in the range of 690–710 nm. A second band of unknown origin appears in the spectrum of specimen 1392. Polarized spectra were measured at room temperature (Fig. 5). There are pronounced differences in the band intensity in different polarization directions, but the band maximum remains at the same wavenumber value indicating a single emitting state.

The luminescence seen at room temperature is relatively weak because of thermal quenching. The luminescence intensity increases rapidly with decreasing temper-

Table 2. Observed wavenumbers of unpolarized room temperature spectra and their assignments

Band	1391	1392	1393	106825	Assignment
ν_1	26 600	26 700	26 700	26 700	$^6A_1(S) \rightarrow {}^4E(D)$
ν_2	24 100	23 800	24 200	23 900	$\rightarrow {}^4T_2(D)$
ν_3	22 700	22 800	22 500	22 600	$\rightarrow {}^4A_1, {}^4E(G)$
ν_4	—	20 800	20 000	20 400	$\rightarrow {}^4T_2(G)$
ν_5	—	19 800			
ν_6	—	16 200	17 500	17 500	$\rightarrow {}^4T_1(G)$

ature and does not reach a saturation brightness at the lowest temperature measured, 78 K (liquid N) (Fig. 6). The fall-off of intensity with temperature is nonlinear and has essentially the same form regardless of whether peak height or integrated intensity is used as a measure. Assuming a simple one phonon–assisted nonradiative decay model for the temperature quenching of the Fe^{3+} luminescence, the decay curve can be fitted to the equation

$$I(T) = \frac{1}{1 + C\exp\left(\frac{\Delta E}{kT}\right)} \tag{3}$$

by setting the phonon energy $\Delta E = 0.056$ eV (450 cm^{-1}). This falls in a region of strong vibrational modes of the feldspar structure. There is an intense Raman line in the orthoclase spectrum at 513 cm^{-1} (White, 1975a) related to a mixed stretch-bend motion of the Si–O–Si bridging bond which might be a reasonable candidate for the phonon coupling the thermal quenching.

Evidence that the luminescence described here and also described from other feldspars by Geake et al. (1973), Geake and Walker (1975), and Telfer and Walker (1975) is due to Fe^{3+} is provided by the close resemblance of the feldspar spectra to the emission spectra of Fe^{3+} in γ-$LiAlO_2$ and $LiAl_5O_8$ in which the Fe^{3+} activator is known to substitute for Al^{3+} in tetrahedral sites (Palumbo, 1971; Melamed et al., 1972; Pott and McNicol, 1972; Neto et al., 1981; and Abritta et al., 1985). However, the lithium aluminate emission bands are resolved into some detailed fine structure including a sharp zero-phonon line at low temperatures. No fine structure was observed in the feldspar luminescence spectra at any temperature.

DISCUSSION

The band assignments are listed in Table 2. The absorption spectra of Fe^{3+} in orthoclase are rather similar to the excitation spectra of Fe^{3+} luminescence in plagioclase reported by Telfer and Walker (1975). There seems little doubt that these bands are due to the crystal-field transitions of the isolated Fe^{3+} ion. There has been some continuing revision of the specified band assignments over the years. Faye's (1969) original assignments were revised by Manning (1970) who assigned ν_1, ν_2, and ν_3 (notation of the present paper) as given in Table 2. A weak band observed at 20 700 cm^{-1} was assigned to the $^6A_1 \rightarrow {}^4T_2(G)$ transition, but the lowest $^4T_1$ level was not observed. Hofmeister and Rossman (1984) added a weak band near 16 000 cm^{-1} to the list and assigned it to the missing $^4T_1(G)$ level. The band assignments in Table 2 are in agreement with Hofmeister and Rossman's assignments.

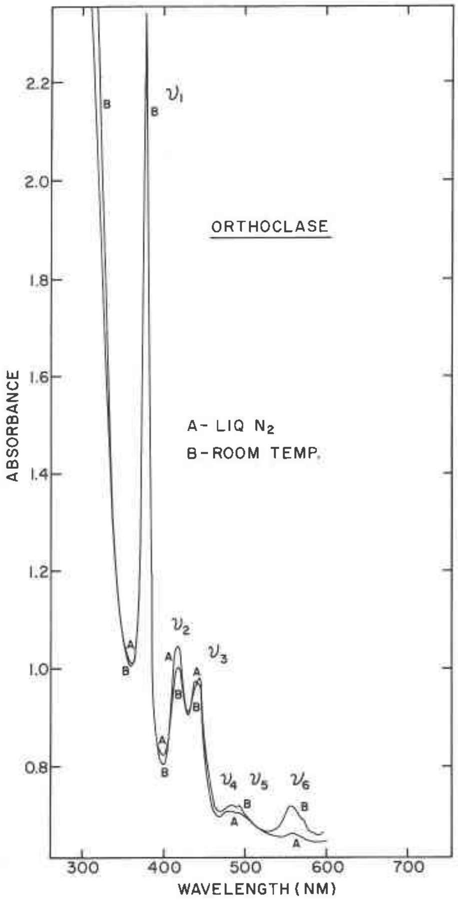

Fig. 2. Spectra of orthoclase specimen 106825 at room temperature and at liquid N temperature. Thickness = 5.5 mm.

The bands labeled ν_1, ν_2, and ν_3 belong to levels that are rigorously independent or only slightly dependent (ν_2) of

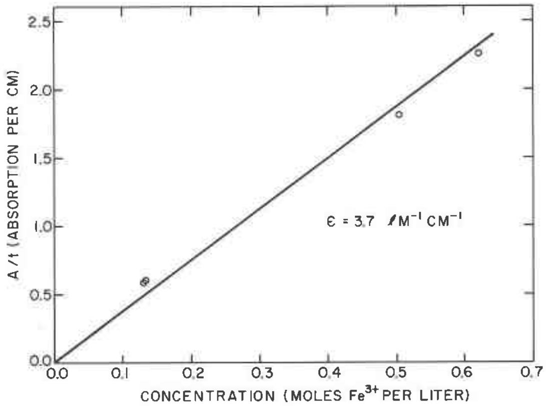

Fig. 3. Beers law plot for the 26 700 (ν_1) band.

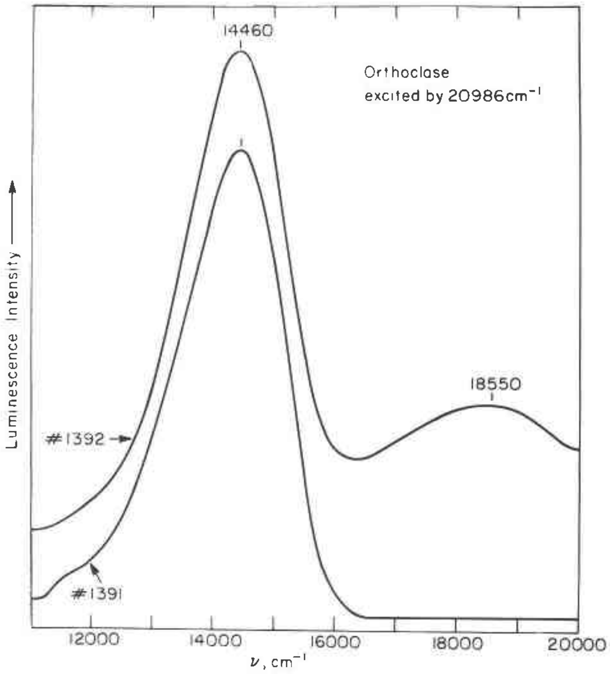

Fig. 4. Unpolarized spectra of two orthoclase specimens at room temperature.

the strength of the crystal field, whereas ν_4, ν_5, and ν_6 are strongly dependent on the crystal field. The observation that the intensities of ν_1, ν_2, and ν_3 increase at low temperature, whereas the intensities of the other three bands decrease, is evidence for the correctness of the assignments. The observation of the luminescence band is further evidence that the weak absorption band labeled ν_6 is the $^4T_1(G)$ level. Emissions from ions with the d^5 electron configuration all take place from this level (White, 1975b).

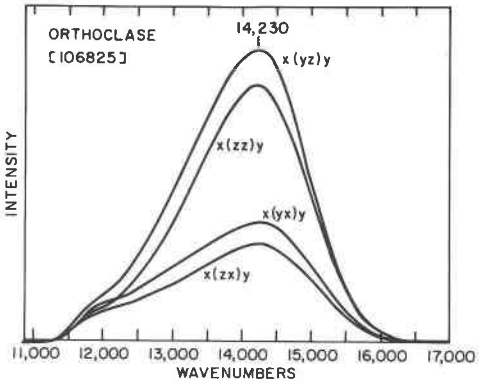

Fig. 5. Polarized spectra for specimen 106825. The labeling of polarization directions is the Porto notation used in Raman spectroscopy. The first symbol is the direction of the exciting laser beam through the oriented crystal of the electric vector of the incident beam and the emerging luminescent beam, respectively, and the final symbol is the direction of the emerging luminescent beam; *x*, *y*, and *z* refer to the indicatrix axes of the crystal.

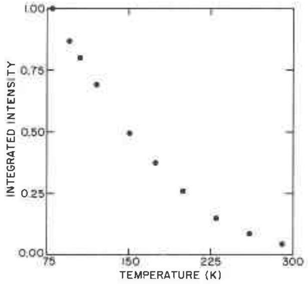

Fig. 6. Temperature dependence of the integrated intensity of the Fe3+ luminescence band.

The emission is offset from the absorption by a Stokes shift of 1500–2000 cm⁻¹, a very reasonable value for these ions in oxide and silicate structures (White, 1975b).

The energies of the field-independent levels $^4E(D)$ and $^4A_1^4E(G)$ can be used to calculate the Racah parameters directly using the solutions of the Tanabe-Sugano matrices (Sugano et al., 1970)

$$\nu_1 = 17B + 5C$$
$$\nu_3 = 10B + 5C. \tag{4}$$

Racah $B = 557$ and Racah $C = 3446$ for specimen 1392, and these values were used to calculate the complete Tanabe-Sugano diagram for the d^5 configuration (Fig. 7). The selection of Dq = 900 cm⁻¹ determines the energy-level

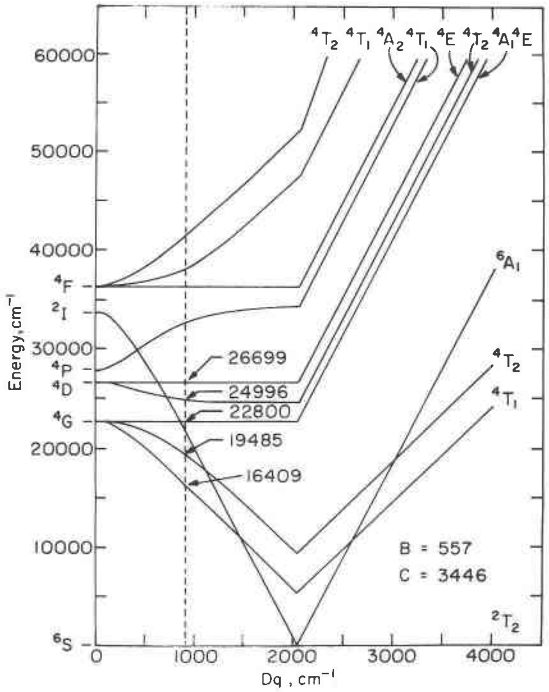

Fig. 7. Calculated Tanabe-Sugano diagram for the d^5 electron configuration assuming the specific values of Racah *B* and *C* found for Fe3+ in orthoclase. The vertical dotted line shows the location of the expected absorption transitions for Dq = 900 cm⁻¹. The numbers given on the diagram are the calculated absorption-band positions.

positions shown in Figure 7. These may be compared with the observed bands listed in Table 2. The good fit confirms the assignments.

The calculated values for the crystal-field parameters are generally as expected for Fe^{3+} on tetrahedral sites. They are in rather good agreement with the theoretical values for the FeO_4^{5-} cluster recently calculated by Sherman (1985). Sherman found $B = 579$ cm^{-1} when calculated from the t_2^4e configuration and $B = 620$ cm^{-1} when calculated from the $t_2^3e^2$ configuration. Dq was estimated to be 823 cm^{-1}.

CONCLUSIONS

The optical absorption spectra and luminescence spectra of Fe^{3+} in the Fe-rich Madagascar orthoclases have been refined and some additional detail on the polarization and temperature dependence provided. Assignments for the various features are listed in Table 2 and confirmed by the good fit to the calculated energy-level diagram of Figure 7. It appears that the deep-red luminescence observed by both UV and electron-beam excitation in many terrestrial feldspars and a few lunar feldspars is indeed due to the $^4T_1 \rightarrow {}^6A_1$ emission of Fe^{3+} on the Al^{3+} sites in the feldspar structure.

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