

U.S. Geological Survey (oral communication). Fabianite contains the same $[\text{B}_3\text{O}_5(\text{OH})]_n^{-2n}$ sheets found in the synthetic $\text{CaB}_3\text{O}_5(\text{OH})$, but in fabianite the Ca is eightfold coordinated, in contrast to the sixfold coordination determined in the synthetic dimorph (Clark *et al.*, 1962). The resulting closer packing accounts for fabianite having a smaller cell volume and greater density than the synthetic compound.

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THE OPTICAL ABSORPTION SPECTRUM OF TETRAHEDRALLY BONDED Fe^{3+} IN ORTHOCLASE

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Recently there has been much interest in the effect of Fe^{2+} and Fe^{3+} on the optical absorption spectra of silicate minerals and on the structural implications of such spectra (*e.g.*, Burns, 1965; White and Keester, 1966;

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Manning, 1967; Faye, 1968; Faye, Manning and Nickel, 1968). It is evident from this work that iron ions are most commonly found in six-coordinate sites especially in ferromagnesian silicates. When both Fe^{2+} and Fe^{3+} are present in appreciable amounts, the spectra can become very complex and difficult to unravel.

It is known that Fe^{3+} also occurs in tetrahedral sites, for example in certain phlogopites (Steinfink, 1962; Faye and Hogarth, 1968) and in a synthetic iron mica (Donnay, Morimoto, Takeda and Donnay, 1964). However, to the author's knowledge there are no good published examples of the detailed spectrum of tetrahedrally bonded Fe^{3+} in an oxygen environment. It is considered that such a spectrum would be of value, particularly for comparison purposes, to workers concerned with the optical properties of silicate minerals.

A lemon-yellow gem-quality specimen of an iron-rich orthoclase from Itrongay, Madagascar, was made available to the author by H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada. Because Fe^{3+} is known to proxy for Al in such material (Deer, Howie and Zussman, 1963, p. 45), it was considered worthwhile to measure its optical absorption spectrum and to present the spectral details, together with transition assignments and certain other interpretations, which follow.

The Itrongay orthoclase is not visibly pleochroic (*i.e.*, spectrally isotropic) therefore a random section (0.37 cm in thickness) was cut from the specimen and polished for spectral measurements. The spectrum, recorded with a Cary model 14 spectrophotometer is shown in Fig. 1.

Fe^{3+} , a d^5 ion, in a cubic field (octahedral and/or tetrahedral) theoretically should give rise to nine relatively weak spin-forbidden transitions from the sextuplet ground state (${}^6\text{S}$) to states arising from the free-ion terms. The energy levels associated with such transitions are shown in Fig. 2.

From Fig. 1 it is apparent that only three principal bands at 26500cm^{-1} , 24000cm^{-1} and 22650cm^{-1} are resolved in the orthoclase spectrum. These can be assigned tentatively to the ${}^6\text{A}_1 \rightarrow {}^4\text{A}_1{}^4\text{E}(\text{G})$, ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2(\text{G})$ and ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1(\text{G})$ transitions respectively. The sharpness of the 26500cm^{-1} band is consistent with it being assigned to the transition to the first field-independent state (Cotton and Wilkinson, 1962; Manning, 1967).

That only the three lowest energy bands representing sextuplet \rightarrow quadruplet transitions are resolved is due to the encroachment into the visible region of the intense background absorption centred in the ultraviolet. It is reasonable to suggest that this intense absorption is due to an $\text{O}^{2-} \rightarrow \text{Fe}^{3+}$ charge-transfer process (Fyfe, 1964).

The transition assignments made above are not unequivocal. If the

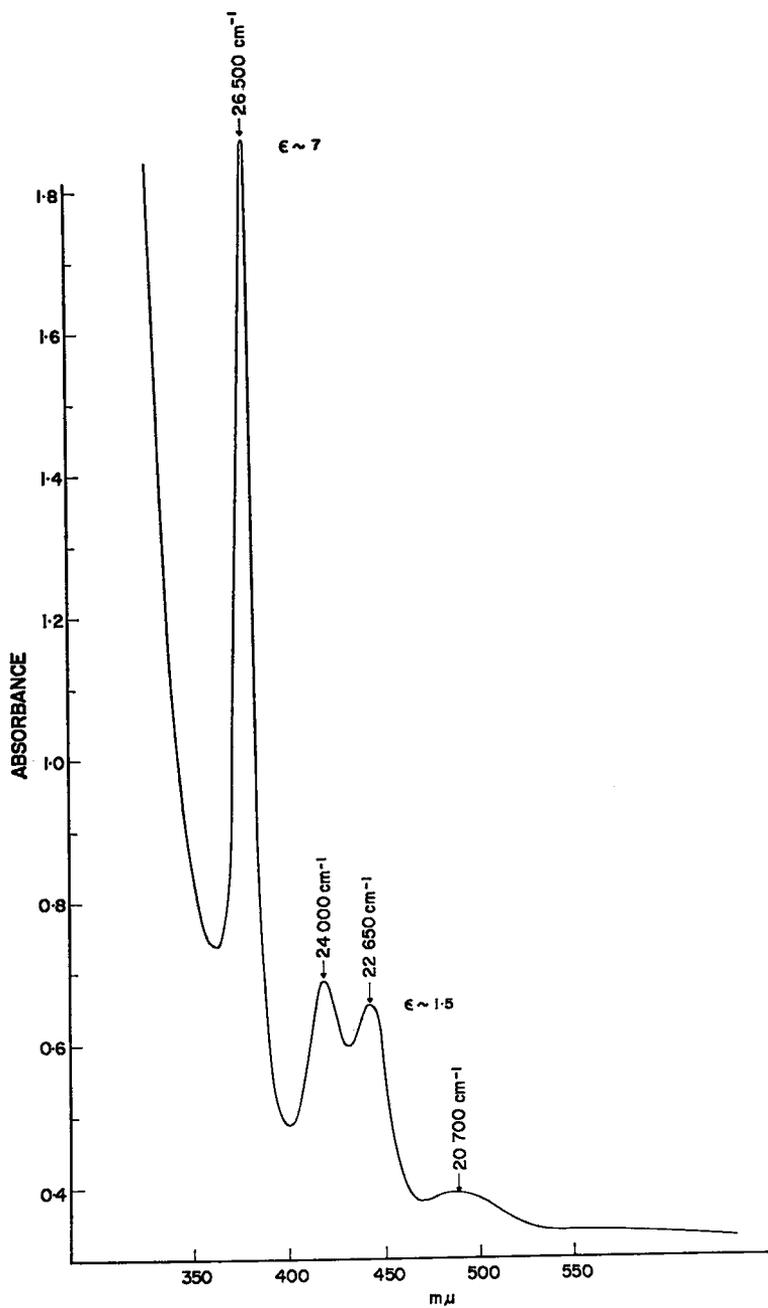


FIG. 1. Unpolarized absorption of Itrongay orthoclase, thickness of 0.37 cm.

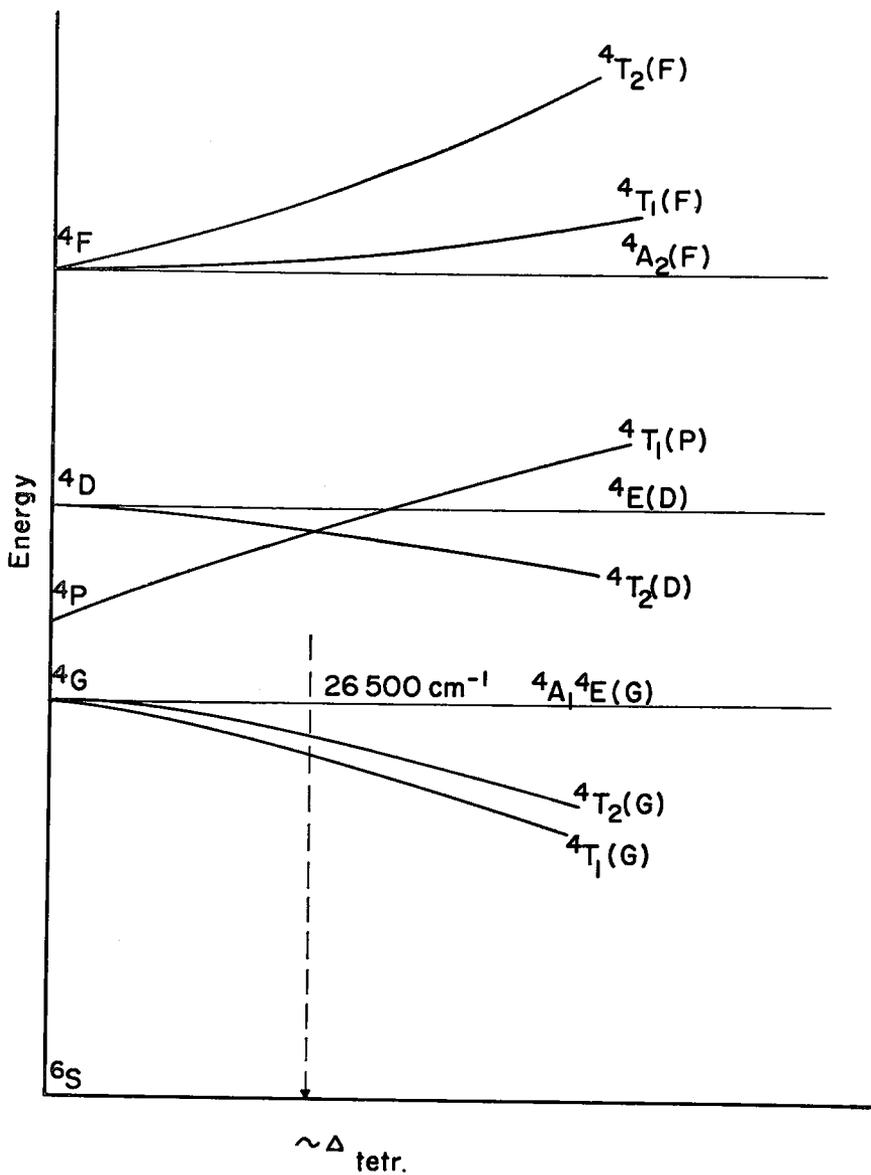


FIG. 2. Energy-level diagram for d^5 ion in a tetrahedral (octahedral) crystal field.

weak ($\epsilon_{\text{Fe}^{3+}} \sim 0.1/\text{mole}\cdot\text{cm}$) feature at 20700 cm^{-1} is taken to be part of the $\text{Fe}^{3+}_{\text{tet}}$ spectrum then it must be assigned to the ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ transition. It follows that the bands at 22650 , 24000 and 26500 cm^{-1} must be assigned to the ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$, $\rightarrow {}^4\text{A}_1{}^4\text{E}$ and $\rightarrow {}^4\text{T}_2(\text{D})$ transitions respectively. However, because of the sharpness of the 26500 cm^{-1} band, its association with the field-independent state (${}^4\text{A}_1$, ${}^4\text{E}$) is preferred.

It is assumed tentatively, that the 20700 cm^{-1} band is due to the presence of traces of a transition metal other than $\text{Fe}^{3+}_{\text{tet}}$. (Transition metal ions, other than d^5 ions, exhibit relatively more intense spin-allowed bands.)

It is of interest to note that the yellow colour of the Itrongay orthoclase is due mainly to the absorption of blue light by the bands at 24000 cm^{-1} and 22500 cm^{-1} , *i.e.*, in the $400\text{--}450\text{ m}\mu$ region of the spectrum.

By correlating the colour with the analyses given for the Itrongay orthoclase by Deer, Howie and Zussman (1963, p. 45), it was assumed that the present specimen contained 1.5% Fe_2O_3 . Extinction coefficients (ϵ) for the $d\text{--}d$ bands were then calculated using the concentration of Fe^{3+} ($\sim 0.5\text{ M}$); these are shown in Fig. 1.

The extinction coefficient for the field-independent band at 26500 cm^{-1} is appreciably higher ($\epsilon \sim 7$) than for the corresponding band in the spectra of octahedrally bonded Fe^{3+} in certain silicates ($\epsilon \sim 1\text{--}2$) (Manning, 1967, 1968; Faye, 1968*a*). This observation is in accord with the general fact that spectral bands of tetrahedrally sited ions are more intense than those of octahedral ones because of the mixing of d - and p -orbitals in the former.

The present orthoclase spectrum, being that of tetrahedrally bonded Fe^{3+} , has potential usefulness as a comparison standard. For example, it has recently proved valuable in a study where the reverse pleochroism of a phlogopite was shown to be due to Fe^{3+} in tetrahedral sites (Faye and Hogarth, 1968).

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A NOTE ON THE UNIT CELL CONSTANTS, AND X-RAY DIFFRACTION POWDER PATTERN, OF PYROBELONITE

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Pyrobelonite, $PbMn(VO_4)(OH)$, is one of several vanadates the structures of which have been determined in this laboratory but for which powder identification data have not yet appeared in the *ASTM Index* (1968). The specimen at our disposal, kindly supplied by Professor C. Frondel, was Harvard 94831 from the type locality, Långban, Sweden. It consists largely of massive to well-crystallized hausmannite in contact with, and cut by, calcite. The pyrobelonite occurs as very fine grains with a few small crystals (commonly $<100 \mu$ in largest dimension) primarily in the hausmannite but at least one was found at an interface with the calcite. The isolation of a reasonable number of crystals, free from hausmannite and calcite, and their authentication by precession photographs, for the purpose of preparing a suitable powder specimen was in progress when Moore (1967) published x-ray diffraction powder data for Långban pyrobelonite. It is a relief, therefore, not to have to sacrifice the very few satisfactory crystals isolated from the Harvard specimen. It is particularly gratifying that Moore not only had access to an adequate supply of good material, but located one sample large