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ON THE OPTICAL SPECTRA OF DI- AND TRIVALENT IRON IN CORUNDUM: A DISCUSSION

G. H. FAYE, *Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.*[1]

INTRODUCTION

The color and pleochroism of blue kyanite (Al_2SiO_5) has been attributed to traces of Ti^{3+} by White and White (1967); however, subsequently, Faye and Nickel (1969) showed that these optical properties could be accounted for more readily on the basis of $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer processes. This writer contends that the latter interpretation is supported by the spectra of iron-bearing corundum reported recently in this journal by Lehmann and Harder (1970). However, the correlation of the spectra of blue kyanite with that of the iron-corundum suggests that aspects of Lehmann and Harder's interpretation of certain of their spectra are open to question.

DISCUSSION

Figure 1 shows the polarized optical spectra of blue kyanite [Figure 1(a)] and Fe^{2+}-corundum [Fig. 1(b)] approximately in the 8,000 to 22,000 cm^{-1} range. It is evident that each absorption envelope is composed of two polarized components; however, only the high-energy band lies in the visible region and it is largely responsible for the colour and pleochroism of the mineral.
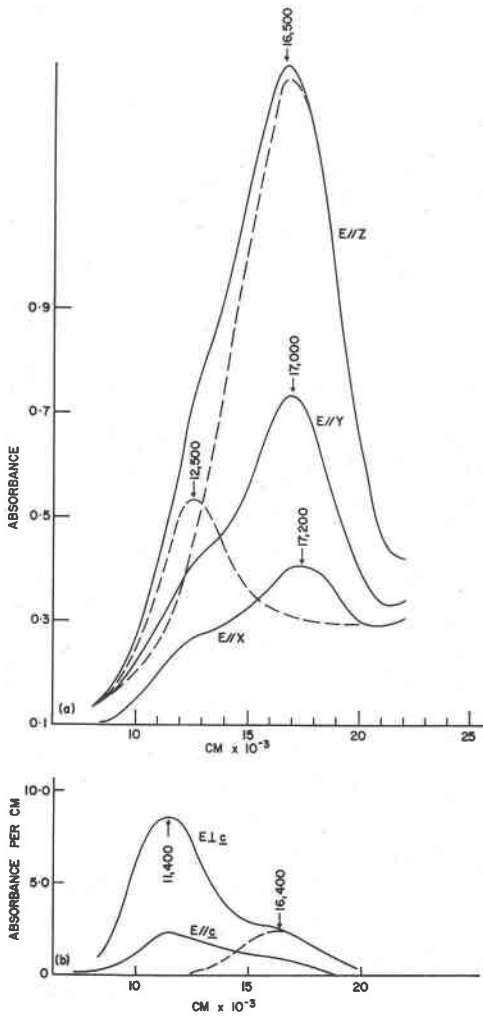
FIG. 1. (a) Polarized spectra of blue kyanite; thickness for $E\|X$ spectrum 0.28 cm; thickness for $E\|Y$ and $E\|Z$ spectra 0.37 cm, (after Faye and Nickel, 1969). (b) Polarized spectra of a pleochroic corundum containing both di- and trivalent iron (after Lehmann and Harder, 1970).

It is to be noted that the original spectra of the two minerals show minor bands, at higher energy, that are due, with certainty, to Fe^{3+} on pseudo-octahedral sites. These spectral features need not be considered further in this discussion.

Faye and Nickel (1969) assigned the band at 12,500-cm^{-1} in the

spectra of blue kyanite to the $^5T_2 \rightarrow ^5E_2$ transition of Fe^{2+} proxying for Al^{3+}. A single polarized absorption band, due to six-coordinate Fe^{2+}, is also found at 12,500-cm^{-1} in the spectra of golden beryl (Grum-Grzhimailo et al., 1962; Wood and Nassau, 1968). The relatively high energy of the transition is consistent with the short Al-O distances in these minerals, i.e., 1.90–1.93 Å for kyanite (Burnham 1963) and 1.90 Å for beryl (Gibbs, Breck, and Meagher 1968). Therefore, because the average Al-O bond distance for corundum is 1.92 Å, it is reasonable to expect that the value of 10 Dq of Fe^{2+} in corundum would not be greater than 12,500-cm^{-2}. However, as will be discussed later, Lehmann and Harder calculated this value to be 13,300-cm^{-1} from the two bands shown in Figure 1(b), both of which were attributed to Fe^{2+}.

It is well established that the color and pleochroism of many silicate (and other) mineral is strongly influenced by polarized $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer bands in the 14,000 to 19,000-cm^{-1} region of the spectrum (for example, see: Hush, 1967; Faye, 1968; Faye et al., 1968; Faye and Nickel, 1970). The charge-transfer process occurs in structures in which adjacent Fe^{2+} and Fe^{3+} ions share octahedral edges and there is possible overlap of t_{2g} orbitals. The intense band from 15,000 to 16,000-cm^{-1} in the $E \| b$ spectrum (E = electric vector) of partially oxidized vivianite is an impressive manifestation of the $Fe^{2+} \rightarrow Fe^{3+}$ process (Hush 1967; Faye et al., 1968). It is in the b direction that lobes of t_{2g} orbitals of adjacent ions can overlap across mutually shared octahedral edges.

Because of the presence of both Fe^{2+} and Fe^{3+} in blue kyanite, and the abundant sharing of octahedral edges (in several directions) in its structrue, the bands in the 16,500 to 17,200-cm^{-1} range of the spectra in Figure 1(a) were also attributed by Faye and Nickel to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process rather than to a split d-d component of Fe^{2+}, or to traces of Ti^{3+}(White and White, 1967).

Qualitatively the spectra of blue kyanite and the iron-corundum in Figure 1 are remarkably similar; therefore it is suggested that they may be of common origin, i.e., the band at 11,400-cm^{-1} is due to the $^5T_2 \rightarrow ^5E_2$ transition of Fe^{2+}, and the band at 16,400-cm^{-1} is due to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process.

Lehmann and Harder argued that both the 11,400- and 16,400-cm^{-1} (or 15,600 in $E \| c$ spectrum) bands are due to the splitting of the excited ^5E state of Fe^{2+} by the Jahn-Teller mechanism, and because of this, dismiss the possibility that the high-energy component could be due to an intervalence transition between Fe^{2+} and Fe^{3+}. It has been shown (Sturge, 1967, p. 191) that the typical energy of an "e" hole is approximately 0.5

eV; however a splitting of 5,000-cm^{-1} is equivalent to a Jahn-Teller energy of approximately 4 eV. Such a discrepancy does not favour the interpretation of Lehmann and Harder.

From the examination of numerous spectra of Fe^{2+}-bearing materials, the author has found that the half-width of typical *d-d* bands is usually in the range 1,500–3,000 cm^{-1}. By comparison then, the 11,400-cm^{-1} band in Figure 1(b) would seem to be rather broad; it is possible, however, that there may be two closely spaced components, possibly arising from the Jahn-Teller mechanism, that could account for this.

The author has recently completed work (to be submitted for publication) which shows that on plotting Dq_{oct} values versus average *M-O* bond distances for a large number of Fe^{2+}-bearing materials, an essentially linear relationship is obtained in the range of bond distances studied (1.90–2.20 Å). Where two bands arising from the splitting of the $^5E_2$ state were observed, the average of their energies was taken as a measure of Dq. It is to be noted that the above linear correlation is obtained even though it is often assumed that the $^5T_2$ level is split by a low symmetry site.

Using such a plot it is estimated that $10Dq$ for corundum is 12,300 ± 300 cm^{-1}. If Lehmann and Harder's spectral assignment is correct, then an anomalously high value of $\sim$14,000 cm^{-1} (average of 11,400 and 16,400 cm^{-1} bands) or 13,300 cm^{-1} (Lehmann and Harder) is obtained. On the other hand, if only the 11,400 cm^{-1} band is attributed to Fe^{2+}, a rather low value of 11,400 cm^{-1} is obtained for 10 Dq. However, this observation, together with the broadness of the 11,400-cm^{-2} band, supports the suggestion that a weak component may exist on the high-energy side of absorption envelope thus putting 10 Dq at a higher value. A similar case is the spectrum of osumilite where a weak "hidden" band significantly affects the value of 10 Dq for six-coordinate Fe^{2+} (unpublished work).

From the crystal structure of corundum (Newnham and De Haan, 1962) it is apparent that there are two kinds of short metal-metal vectors, crossing octahedral edges, along which intervalence charge-transfer between adjacent Fe^{2+} and Fe^{3+} can take place. One kind of vector 2.65 Å in length, is coincident with *c* while the other kind, 2.79 Å in length, is very approximately perpendicular to *c*. There are three times as many of the latter kind of vector as the former, therefore this may well account for the observation that the $E \perp c$ spectrum of corundum in Figure 1(b) is approximately three times as intense as the $E \| c$ spectrum.

According to Lehmann and Harder, the high-energy band, which we attribute to $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer has its maximum at 16,400-cm^{-1}

in the $E \perp c$ spectrum and at 15,600-cm^{-1} in the $E \| c$ spectrum. This variation in energy is consistent with the length of the metal-metal vectors in the two crystallographic directions. At least in part, it is to be theoretically expected that the shorter the distance between the interacting centers the lower should be the energy of the intervalence transition. Such a relationship has been found for the $Fe^{2+} \rightarrow Fe^{3+}$ bands in the spectra of a number of amphiboles (Fayes and Nickel, 1970).

Although the total iron concentration of the blue kyanite (approx. 0.15 percent) studied by Faye and Nickel was lower than that (approx. 0.7 percent) of the corundum specimen of Lehmann and Harder, the $Fe^{2+} \rightarrow Fe^{3+}$ band of the former is considerably more intense than that of the latter. However the kyanite was highly zoned or banded, indicating a clustering of iron ions. Therefore, the concentration of interacting ions was probably higher in the kyanite than in the corundum.

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