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RELATIONSHIP BETWEEN CRYSTAL-FIELD SPLITTING PARAMETER, "Δ_{VI}", AND M_{host}-O BOND DISTANCE AS AN AID IN THE INTERPRETATION OF ABSORPTION SPECTRA OF Fe^{2+}-BEARING MATERIALS

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Abstract

The electronic absorption spectra of Fe^{2+}-bearing minerals are often complicated by the presence of $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer bands and by splitting arising from the occupation, by Fe^{2+}, of several non-equivalent sites, from site distortions, or from the Jahn-Teller mechanism; consequently, spectral interpretations are often in doubt. This work shows that on plotting "Δ_{VI}" (average energy of bands associated with the excited ^5E state) versus M_{host}-O bond distance for a large number of Fe^{2+}-bearing materials, an essentially linear relationship is obtained within the range of bond distances studied (1.9-2.2 Å). Splittings of the $^5T_2$ state are ignored. It is considered that the "reference curve" of "Δ_{VI}" *vs.* *M*-O is valuable in: establishing the validity of band assignments by permitting a distinction between "*d-d*" and *M-M* charge-transfer bands; finding hidden, weak, spin-allowed "*d-d*" bands; estimating average *M*-O bond distance for unknowns; and in detecting "anomalies" in bonding of Fe^{2+} in certain structures.

Introduction

The electronic absorption spectra of many silicate minerals, oxides and other materials containing Fe^{2+}, and possibly Fe^{3+}, in a pseudo-octahedral array of oxygens (O^{2-}, OH^-, H_2O, SiO_4^{-}, AlO_4^{5-}, *etc.*) have been studied extensively; however, the literature indicates that there are still many problems associated with their interpretation.

Rather than the single absorption band due to the spin-allowed transition, $^5T_{2g} \rightarrow {}^5E_g$ (^5D), expected for Fe^{2+} in a regular octahedral crystal field, the spectra of iron-bearing materials often contain a perplexing multiplicity of features (*e.g.* Burns 1970). These arise through the occupation, by Fe^{2+}, of several non-equivalent coordination sites, from site distortions, or possibly from the dynamic Jahn-Teller mechanism. Additional complications sometimes arise because of the difficulty in distinguishing between "*d-d*" bands of Fe^{2+} and those due to $Fe^{2+} \rightarrow Fe^{3+}$ intervalence charge-transfer (*e.g.* Wilkins, Farrell & Naiman 1969; Burns 1970 (p. 72); Faye, Manning & Nickel 1968; Faye 1971).

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TABLE 1. BOND DISTANCES AND SPECTRAL DATA FOR Fe^{2+}-BEARING MINERALS

Material	Range of bond distance Å	Av. bond distance Å	Reference	Av. "Δ_{VI}" cm^{-1}	~ Splitting of excited cm^{-1}*	Reference for spectral data
Beryl	Nil	1.90	Gibbs *et al.* (1968)	12,500	—	Wood & Nassau (1968)
Kyanite	1.90-1.93	1.92	Burnham (1963)	12,500	—	Faye & Nickel (1969)
Vivianite Fe_I and Fe_{II}	1.97-2.00	1.98	Faye (1968)	10,000	4,100	Townsend & Faye (1970)
Tourmaline Mg-site	2.02-2.12	2.05	Buerger *et al.* (1962)	11,100	5,000-6,000	Faye, Manning & Nickel (1968) and unpublished work
Bronzite M_1		2.08**		10,000	2,600	Burns (1970) p. 91
MgO	Nil	2.10	Bragg & Claringbull (1965)	10,300	1,800 (unpolarized)	Jones (1967)
Sinhalite	2.04-2.21	2.10	Fang & Newnham (1965)	10,150	1,300	Farrell & Newnham (1965)
Forsterite M_1	2.08-2.14	2.10	Birle *et al.* (1968)	10,000	3,700	Burns (1970) p. 80
Riebeckite M_1 and M_3 (Crocidolite)	2.10-2.12	2.11	Whittaker (1949)	10,200	1,500	Faye & Nickel (1970) and unpublished work
Actinolite M_1, M_2 and M_3	2.02-2.16	2.11	Zussman (1955)	9,900	2,600	Burns (1970) p. 101
Biotite Fe_I and Fe_{II}	2.07-2.13	2.11	Donnay *et al.* (1964)	10,300	2,100 (unpolarized)	Faye (1968)
Cordierite Mg/Fe-site	2.11-2.12	2.12	Gibbs (1966)	9,800	2,100	Faye *et al.* (1968)
Ludlamite Fe_I and Fe_{II}	1.99-2.30	2.12	Ito & Mori (1951)	9,100	4,100 (unpolarized)	this work
$Fe(NH_4)_2(SO_4)_2 . 6H_2O$	2.09-2.16	2.13	Montgomery *et al.* (1967)	9,600	2,400 (unpolarized)	Cotton & Meyers (1960)
$FeSiF_6 . 6H_2O$	Nil	2.15	Hamilton (1962)	9,700	1,400 (unpolarized)	Jones (1967)
Osumilite	Nil	2.15	Brown & Gibbs (1969)	9,600	1,800 (unpolarized)	this work
Forsterite M_2	2.06-2.22	2.14	Birle *et al.* (1968)	9,600	—	Burns (1970) p. 80
Orthoferrosilite M_1	2.09-2.20	2.15	Burnham (1966)	9,600	2,200	Burns (1970) p. 89
Fayalite M_1	2.12-2.23	2.16	Birle *et al.* (1968)	9,500	3,400	Burns (1970) p. 81
Fayalite M_2	2.07-2.23	2.18	Birle *et al.* (1968)	9,300	—	Burns (1970) p. 81
Axinite Fe-site	1.97-2.53	2.20	Ito & Takeuchi (1952)	8,700	1,500	this work
Bronzite M_2		2.21**		8,200	5,600	Burns (1970) p. 88
Orthoferrosilite M_2	2.01-2.62	2.24	Burnham (1966)	7,900	5,900	Burns (1970) p. 89

* Estimated by the author of this work.
** Estimated by the author from the structure of hypersthene, Fs_{53} (Ghose 1965).

This paper shows how the interpretation of such absorption spectra may be facilitated through the use of a simple plot of the crystal-field splitting parameter versus the average M_{host}-O bond distance of the six-coordinate Fe^{2+} site.

Experimental

Specimens of ludlamite (Blackbird mine, Lemhi Cty., Idaho), osumilite (MacKenzie Pass, Lane Cty., Oregon), and axinite (La Olivia scheelite mine, Baja California, Mexico) were obtained through the courtesy of Mr. H. R. Steacy, curator of the reference series of the National Mineral Collection, Geological Survey of Canada.

Absorption spectra of single crystals of these minerals were measured by the microscope-spectrophotometer technique as in previous work (Faye & Nickel 1970) and are shown in Fig. 4, 5, and 6.

Most of the spectral data in Table 1 were obtained from previously published polarized spectra. Because the position (energy) of absorption bands often varies with crystallographic direction, the maximum values of the splitting of the ^5E state can be obtained only from polarized spectra. Table 1 shows that some unpolarized spectra were also used in the present work. Even though these may not give the maximum splitting of the excited states, they are as useful as polarized spectra for estimating "Δ_{VI}". (See Fig. 1 for distinction between "Δ_{VI}" and Δ_{VI} and Δ_{oct}).

The values of "Δ_{VI}" and the spectral splittings listed in Table 1 were all estimated by the author.. Although some features in certain spectra occur as shoulders rather than discrete bands, it is assumed that their energy can be estimated to within ± 200 cm^{-1}.

To obtain the line of best fit for Figures 2 and 3, the data of Table 1, excluding those for vivianite and ludlamite, were treated by the least-squares method.

Discussion

In most materials, especially ferromagnesian silicates, Fe^{2+} is located on six-coordinate sites that are appreciably distorted from octahedral symmetry. Bond lengths may differ by as much as 0.6 Å within a given polyhedron (*e.g.* orthopyroxene) ; similarly, O-*M*-O bond angles may deviate from orthogonality by as much as 30° (*e.g.* cordierite).

The manner in which the crystal-field states for a d^6 ion such as Fe^{2+} are split (degeneracy lifted) as the symmetry of the site is lowered is

shown quantitatively in Fig. 1. Such energy level diagrams do not give quantitative information about the extent of splitting.

With the possible exception of the M_2 site spectra of orthopyroxene (White & Keester 1967), spectral bands due to transitions from the ground state to excited states (B and E in Fig. 1) are not observed because of their low energy (Burns 1970, p. 91), and little is known about the magnitude of the splitting of the lower levels. From Fig. 1 it is evident that the upper ^5E state is split by crystal fields having other than octahedral or trigonal symmetry, consequently at least two spectral features in the visible or near infrared should be expected for Fe^{2+} in most distorted six-coordinates sites — this is indeed the case (see Burns 1970 for example).

Although the mechanisms responsible for orbital (energy) splittings are not an important aspect of the present work, it is of interest to note, from Table 1, that the magnitude of the splitting of the excited ^5E_g or ^5E level does not correlate well with the extent of the static distortion of the Fe^{2+} site. (*cf.* tourmaline and vivianite with bronzite M_2 and orthoferrosilite M_2 for example).

In previous unpublished work by the author, it was found that a linear correlation exists between the crystal-field splitting parameter, Δ_{VI}, for six-coordinate Ni^{2+} and the average M_{host}-O distance for a number of materials. Similarly, Burns (1965, 1970a) has shown, for certain series of ferromagnesian silicates, that Δ_{VI} for Fe^{2+} decreases linearly as the Fe content of the mineral increases. This is, of course, a manifestation of the increasing bond lengths of the Fe^{2+}-bearing sites and is to be expected from electrostatic principles.

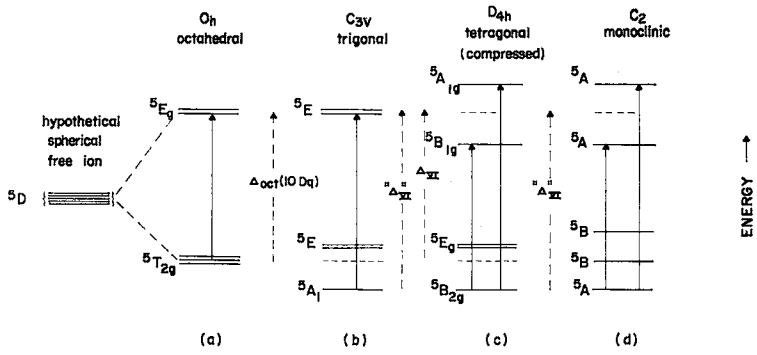

FIG. 1. Energy level diagram for Fe^{2+}_{VI} showing qualitatively how the degeneracy of the crystal-field states is lifted by lowering the site symmetry. Observed transitions are indicated by arrows. The way in which "Δ_{VI}" is estimated is also shown.

From Fig. 1 it can be seen that there is a problem in determining Δ_{VI} from the spectra of materials containing Fe^{2+} in sites of trigonal, tetragonal, or monoclinic symmetries. As indicated earlier, this is due largely to the difficulty in estimating the magnitude of the splittings of the crystal field states derived from the ${}^5T_{2g}$ level in O_h. Nevertheless, certain workers have made such estimates (*e.g.* White & Keester 1967 ; Burns 1970 ; Lehmann & Harder 1970) and have given corresponding crystal-field splitting parameters which correspond to Δ_{oct} or Δ_{VI}.

If it is assumed that the low-symmetry states derived from ${}^5T_{2g}$ in O_h (Fig. 1) are appreciably split and if the ground state is lower than the baricentre of the set of three levels by more than 300-400 cm^{-1}, then it is not possible to obtain meaningful values of Δ_{oct} or Δ_{VI} directly from optical absorption spectra ; therefore, a useful correlation between the strength of the crystal field and the average bond distance of the Fe^{2+} site cannot be made. However, if the low-level splitting is small, or similar, for most Fe^{2+}-bearing materials, then it seems reasonable to expect (on the basis of previously mentioned work on Ni^{2+}-bearing materials and on that of Burns (1965, 1970a)) the existence of a linear relationship between the average energy of the experimentally measured levels derived from the upper ${}^5E_g$ or ${}^5E$ state and the average M_{host}-O bond distance. (Note from Fig. 1 that one spectral band is to be expected from the trigonal case and two for the tetragonal and monoclinic cases.)

Accordingly, spectral data (Table 1) in the visible and near infrared regions for a number of materials were obtained from the literature and from the author's own work and these were plotted against appropriate bond distances to give Figs. 2 and 3. The crystal-field splitting parameter has been symbolized "Δ_{VI}" to distinguished it from the commonly used Δ_{oct} or 10 Dq (Fig. 1).

From Fig. 2 and 3 it is apparent that an essentially linear correlation is obtained, with energy deviations exceeding 400 cm^{-1} for only the two phosphates, vivianite and ludlamite, and for $Fe(NH_4)_2(SO_4)_2.6H_2O$ and bronzite M_1 in Fig. 1 only. Such a "reference" curve has a number of interesting implications in the interpretation of the absorption spectra of Fe^{2+}-bearing materials ; these will be discussed subsequently in detail.

Comments on bond distances

In Figure 2 the "Δ_{VI}" values of Table 1 are plotted against the average M_{host}-O bond distance. Although a linear correlation is obtained, the distances are probably unrealistic for the sites in which Fe^{2+} substitutes for Al^{3+} or Mg^{2+} in low concentrations. Although the actual average

Fe_{VI}-O bond distances for such materials are unknown, they must vary smoothly over a range of values dictated largely by the difference between the ionic radii of Fe^{2+} and the host cation, and by the extent of substitution. For example, the overall average bond distances of the M_1 and M_2 sites of forsterite (Fa_{10}) and fayalite (Fa_{100}) are 2.12 Å and 2.17_5 respectively. As expected, the difference of 0.05_5 Å closely reflects the 0.06 Å difference between the ionic radius of Fe^{2+} (0.86 Å) and Mg^{2+} (0.80 Å) (Whittaker & Muntus 1970). Thus, it is observed that there is a linear correlation between cell parameters and absorption-peak maxima in the forsterite-fayalite series, for example (Burns 1970a).

Using the known average bond lengths of 2.13, 2.13, 2.15 and 2.16 Å for $FeSO_4.7H_2O$, $Fe(NH_4)_2(SO_4)_2.6H_2O$ and FeO, respectively, an overall average of 2.14 Å is obtained as an arbitrary standard for the comparison of the average bond distances of the FeO_6 pseudo-octahedra in the materials considered in this paper.

From the above, it is reasonable to assume that in materials in which Fe^{2+}, in low concentrations, replaces Mg^{2+} or Al^{3+}, the average Fe_{VI}-O bond distances are less than 2.14 Å but greater than the appropriate Mg_{VI}-O or Al_{VI}-O distances. Therefore, in plotting the spectral data of Fig. 3, the average M-O bond distances for cordierite, actinolite, forsterite M_1, bronzite M_1, sinhalite, MgO and tourmaline have all been arbitrarily

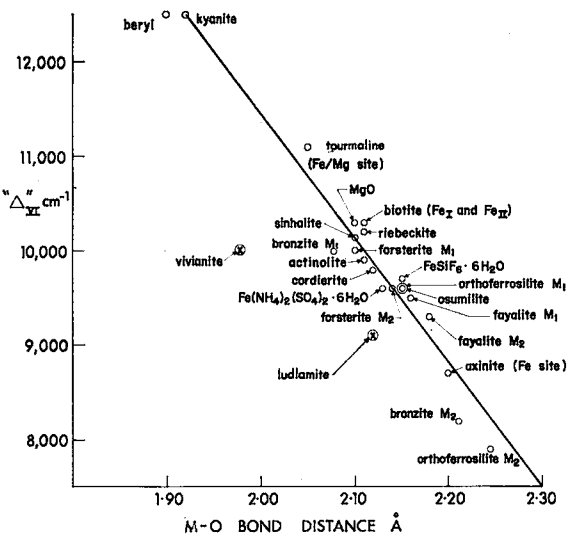

FIG. 2. "Δ_{VI}" versus M(unmodified)-O bond distance.

increased by 0.03 Å (*i.e.*, half the difference between the radii of Fe^{2+} and Mg^{2+}). On the same basis, *M*-O bond distances for beryl and kyanite have each been increased by 0.12 Å. Previous workers (Orgel 1961 ; Lehmann & Harder 1970) have also used the difference between ionic radii in similar studies. It is realized that a more meaningful "correction" would take into account the degree of substitution of Fe^{2+} for Mg^{2+} or Al^{3+}.

The *M*-O distances for biotite, riebeckite, vivianite, ludlamite and $Fe(NH_4)_2SO_4.6H_2O$ were left unchanged because they are essentially actual Fe-O distances.

No change was made for materials whose average *M*-O distances are larger than 2.14 Å because undoubtedly Fe^{2+} is easily accommodated in such sites. In this regard it is interesting to note, as an example, that the average bond distance of the large M_2 site of the orthopyroxenes changes by only 0.02 Å in going from hypersthene (Fs_{53}) to orthoferrosilite (Fs_{100}).

Despite the use of some modified bond distances, a linear plot is also obtained in Fig. 3 ; however, the slope of the line is appreciably greater than that of Fig. 2, and perhaps coincidentally, this results in a better fit

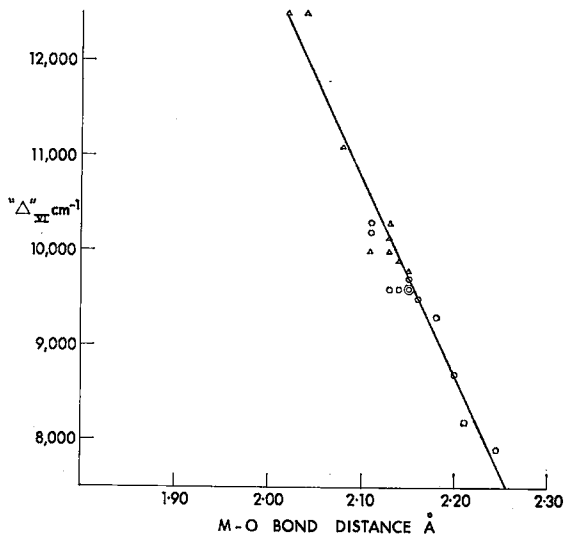

FIG. 3. "Δ_{VI}" versus *M*-O bond distance.

Δ — represents cases where bond distances have been increased by 0.03Å(Mg-sites) or 0.12Å(Al-sites).
O — represents cases where bond distances have not been changed. The data for vivianite and ludlamite are not shown for the reasons given in the text on these minerals.

for the spectral data of bronzite M_2 and orthoferrosilite M_2. Regardless of which line is used for comparative purposes, the implications are the same, as will be seen below.

Comments on interpretation of spectra of specific minerals

Allusion was made previously to problems and uncertainties in the interpretation of the electronic absorption spectra of some iron-bearing minerals. However, by utilizing the "reference" curves of Figs. 2 or 3, it is considered that certain of these problems may be resolved; in addition, the interpretation of new spectra may be facilitated. Discussion of the spectra of specific minerals follows.

Tourmaline — The absorption spectra of blue and green tourmalines are dominated by two bands at ~14,000 cm^{-1} and 8,000-9,000 cm^{-1}. Recent works by Faye, Manning & Nickel (1968) and Wilkins, Farrell & Naiman (1969) are in agreement that the latter peak is a "*d-d*" band of Fe^{2+}. However, Faye *et al.* proposed that the 14,000-cm^{-1} band was due to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process which influences the spectra of many other ferromagnesian silicates (see also Faye & Nickel 1970). However, Wilkins *et al.* (1969) argued that both the spectral features were due to the ${}^5T_2 \rightarrow {}^5E$ transition with the ${}^5E$ state split by structural distortions, or possibly by the dynamic Jahn-Taller mechanism.

From Figures 2 and 3 and Table 1, it is now clear that the latter interpretation is to be favoured. Because the average bond distance of the Mg/Fe^{2+}-site (trigonal brucite units) of tourmaline is 2.05 Å (2.08 Å for Fig. 3) a "Δ_{VI}" value of ~11,000 cm^{-1} is expected. Indeed, if the energies for the two spectral bands are averaged for a number of blue and green tourmalines, a value of 11,100 cm^{-1} is obtained.

Interestingly, it is also apparent that the 14,000-cm^{-1} band cannot be due to Fe^{2+} located on the smaller Al-site of tourmaline because such a high value of "Δ_{VI}" is not appropriate for a site having an average bond distance of ~2.0Å (Fig. 2).

The magnitude of the splitting of the ${}^5E$ state of tourmaline spectra is puzzling. Townsend (1970), using the concepts of Sturge (1967), has pointed out that a splitting of 5,000-6,000 cm^{-1} is too large to be accounted for by the dynamic Jahn-Teller mechanism. On the other hand, the Mg-site of tourmaline is appreciably less distorted than six-coordinate sites of some other materials, listed in Table 1, whose spectra exhibit much smaller splittings (*e.g.*, sinhalite, actinolite, bronzite M_1, forsterite M_2). The spectrum of the phosphate, vivianite, whose Fe^{2+} sites are very regular, also exhibits a very large splitting; therefore, for certain materials at least, there must be some kind of dynamic distorting mechanism that is not well understood.

Osumilite — Osumilite is a framework silicate that resembles cordierite (Brown & Gibbs 1969). As in cordierite, Fe^{2+} is accommodated in pseudo-octahedral sites, while Fe^{3+} occupies tetrahedral sites.

Figure 4 shows the unpolarized spectrum of a basal section of osumilite, the components of which have been resolved with a Dupont curve resolver. The assignments made for each of the features are also indicated.

The intense, broad band at 15,000 cm^{-1} is analogous to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer band proposed for the polarized spectra of cordierite (Faye, Manning & Nickel 1968). The polarization properties of the 15,000-cm^{-1} band in unpublished osumilite spectra are fully in accord with this interpretation. The bands at 22,000 cm^{-1} and 19,000 cm^{-1} are attributed to tetrahedrally coordinated Fe^{3+} and these correspond to similar feasures for tetrahedral Fe^{3+} in phlogopite (Faye & Hogarth 1969).

The "*d-d*" bands of six-coordinate Fe^{2+} have maxima at 10,500 cm^{-1} and 8,700 cm^{-1}. In the "raw" unresolved spectrum only the former is obvious; consequently in preliminary work a value of 10,500 cm^{-1} was taken for "Δ_{VI}" of osumilite. From Fig. 2 or 3 it is evident that such a value is anomalously high for a mean bond distance of 2.15 Å; however, if it is averaged with the weaker 8,700-cm^{-1} band which is isolated by curve resolving, a value of 9,600 cm^{-1} is obtained. Thus the possible importance

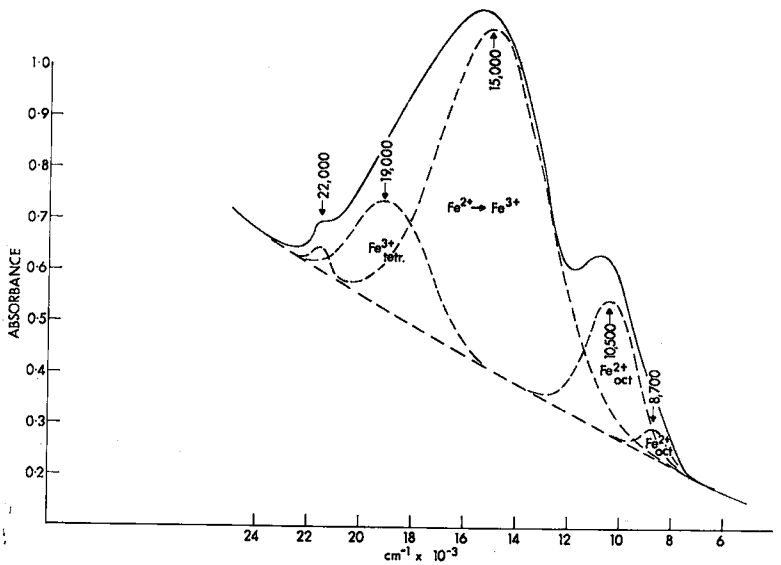

FIG. 4. Unpolarized spectrum of a basal section of osumilite; thickness ~ 0.01 cm.

of weak "hidden" bands in making interpretations is emphasized by the case of osumilite. As we will see, this may also be an important matter in the interpretation of the spectra of Fe^{2+}-bearing corundum.

It is worth noting that the spectral splitting of 1,800 cm^{-1} for osumilite is similar to those for $FeSiF_6.6H_2O$ and MgO, because the three materials all have uniform bond distances (Table 1).

Cordierite — Conflicting interpretations of the polarized spectra of cordierite have also been made. The principal absorption bands, one in the visible region at 17,000-18,000 cm^{-1}, and two in the near infrared region at ~ 10,500 cm^{-1} and 8,500 cm^{-1} were all assigned to Fe^{2+} by Newnham & Farrell (1967). Alternatively, Faye *et al.* (1968) assigned the visible band to $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer and only the two infrared bands to six-coordinate Fe^{2+}. Again, using arguments similar to those above, it can be seen that the latter interpretation must be favoured because a "Δ_{VI}" value of ~ 9,800 cm^{-1} is consistent with the plots in Figures 2 and 3. Newnham and Farrell's assignment leads to an unacceptably high value of ~ 13,000 cm^{-1} for "Δ_{VI}".

The author has also examined the polarized spectra of a high-iron cordierite (sekaninaite) containing 13.7% Fe. "Δ_{VI}" for this material is 9,200 cm^{-1}, a value in accord with the somewhat longer Fe-O distances expected for sekaninaite.

Corundum — Recently, a debate over the interpretation of the polarized absorption spectra of corundum has arisen (data not given in Fig. 2 and 3 or in Table 1). Lehmann & Harder (1970) attributed the two principal bands at 16,400 cm^{-1} and 11,400 cm^{-1} (average 14,400 cm^{-1}) to six-coordinate Fe^{2+} and the large splitting was claimed to be due to the Jahn-Teller mechanism. Lehmann & Harder estimated the crystal-field splitting parameter, Δ_{VI}, to be 13,300 cm^{-1} for Fe^{2+}. From Fig. 2 (unmodified bond distances) this value seems to be inordinately high for the average Al-O bond distance of 1.92 Å for corundum (compare with beryl and kyanite in Fig. 2). Faye (1971) has therefore proposed that the 11,400-cm^{-1} band and a weaker "hidden" component at somewhat higher energy are those belonging to Fe^{2+} and that the corresponding "Δ_{VI}" value is probably not greater than 12,500 cm^{-1}. Faye also argued that the 16,400-cm^{-1} band of the corundum spectrum is possibly due to the $Fe^{2+} \rightarrow Fe^{3+}$ charge-transfer process which influences the spectra of kyanite, cordierite, osumilite and other minerals.

Axinite — The Fe^{2+}-site of axinite is highly distorted (Table 1), therefore it is possible that the large separation of spectral bands in Fig. 5 is due to the splitting of the ^5E state; however, this leads to an anomalously low value of ~ 7,000 cm^{-1} for "Δ_{VI}".

An alternative interpretation is suggested by the "Δ_{VI}" *vs.* *M*-O plot. If only the bands at 9,400 cm^{-1} and 7,900 cm^{-1} are attributed to six-coordinate Fe^{2+}, the resulting value of 8,700 cm^{-1} for "Δ_{VI}" gives an excellent fit in Fig. 2 and 3.

In axinite there is an unusually large Al tetrahedral site with a mean bond distance of 2.08 Å (Ito & Takeuchi 1952). It is possible, therefore, that Fe^{2+} is also accommodated on this site and the band system at 5,050 cm^{-1} is due to the ${}^5E \rightarrow {}^5T_2$ transition of pseudo-tetrahedral coordinated Fe^{2+}. Using the well-known relationship $\Delta_{tetra} \simeq \frac{4}{9}\Delta_{oct}$ and Fig. 2 or 3, it is calculated that such a transition should occur at 4,700-5,000 cm^{-1} — in good agreement with the observed value.

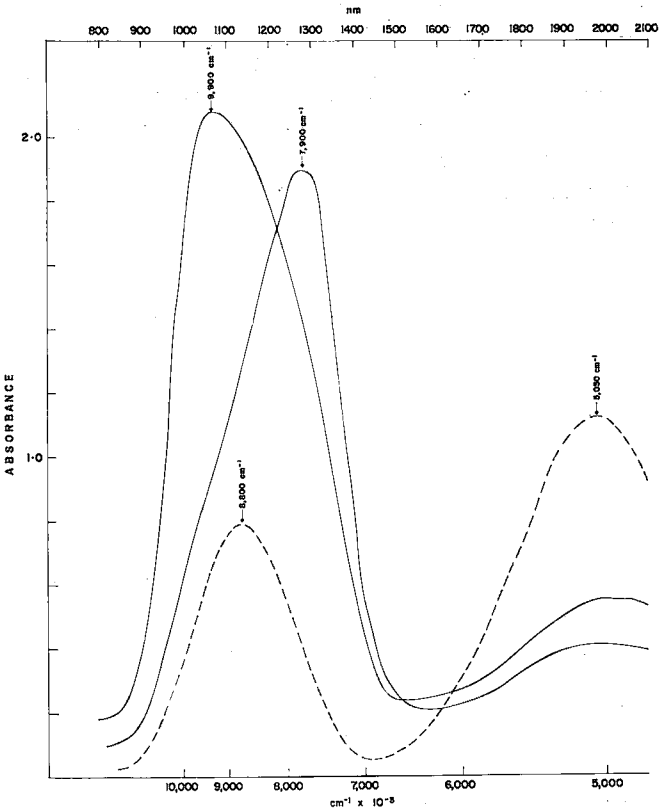

FIG. 5. ———— polarized spectra of a section cut perpendicular to $(0\bar{0}1)$ face of a crystal of axinite; thickness 0.035 cm.
- - - - - - - - unpolarized spectrum of irrational section of crystal of axinite; thickness 0.074 cm.

Olivines and orthopyroxenes — Burns (1970) has discussed the polarized absorption spectra of the olivine and orthopyroxene series in detail. He calculated Δ_{oct} values and crystal-field stabilization energies for the M_1 and M_2 sites of both the Mg-rich and Fe-rich members.

The relatively large distortion, especially of the M_2 sites of both series of minerals, is assumed to lead to extensive splitting of the t_{2g} group of orbital energy levels : 1,860 cm^{-1} for olivines and 3,100 cm^{-1} for orthopyroxenes. Because the ground state for Fe^{2+} on these sites is considered to be appreciably separated from the baricentre (see Fig. 1) of the lower set of orbital energy levels, the resulting Δ_{oct} values calculated by Burns for the M_2 sites are 1,300-1,500 cm^{-1} lower than the corresponding "Δ_{VI}" value in this work.

The Δ_{oct} values of Burns for the M_1 and M_2 sites are rather widely scattered when plotted against the appropriate M-O values. This together with the observation that the "Δ_{VI}" 's for the olivines and orthopyroxenes correlate well with those of many other minerals whose sites are not highly distorted (Fig. 2 and 3), suggest that, unless the magnitude of splitting of the crystal field states arising from $^5T_{2g}$ can be firmly established, caution should be exercised in calculating crystal-field stabilization energies for Fe^{2+} sites from spectral data.

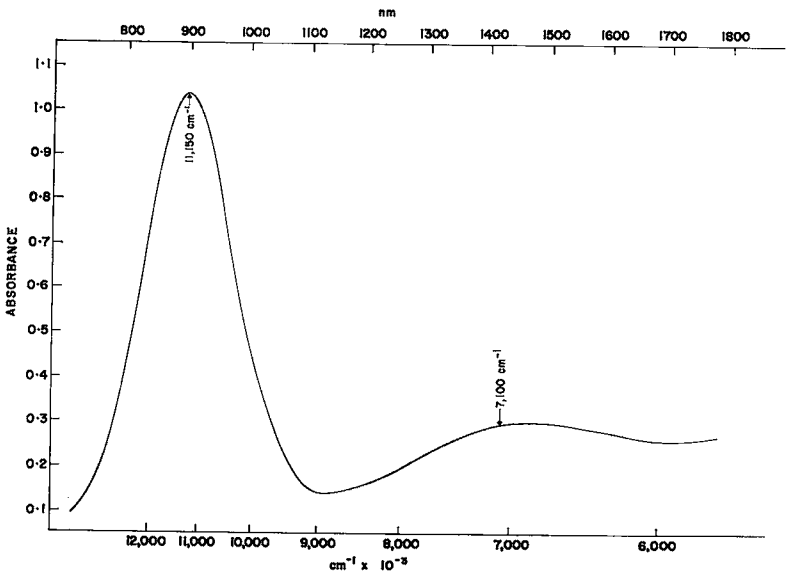

FIG. 6. Unpolarized spectrum of a cleavage tablet of ludlamite; thickness ~ 0.01 cm.

Figures 2 and 3 suggest that the crystal field experienced by Fe^{2+} in the orthopyroxenes is weak relative to other ferromagnesian silicates.

Vivianite and ludlamite — Vivianite ($Fe_3(PO_4)_2.8H_2O$) is especially interesting because of its large spectral band splitting ($\sim 4{,}100\ cm^{-1}$), the regularity of its octahedral sites and the short average Fe-O bond distance (1.98 Å). From Fig. 2 it is evident that the crystal-field splitting parameter (in this case Δ_{oct} of Fig. 1(a) should apply) for Fe^{2+} is unusually low considering the small sites in vivianite. Annabergite, ($Ni_3(AsO_4)_2.8H_2O$), is isostructural with vivianite and unpublished work by the author has shown that Δ_{oct} for Ni^{2+} in this mineral is $\sim 1{,}000\ cm^{-1}$ less than expected for Ni^{2+} bonded to six oxygens.

Hydrogen bonding between adjacent H_2O groups is considered to be important in stabilizing the structure of vivianite (Mori & Ito 1950) and, presumably, annabergite also. It is possible, therefore, that such bonding weakens the crystal field around the M^{2+} ions in these minerals and correspondingly low Δ_{oct} values are observed.

Ludlamite, $Fe_3(PO_4)_2.4H_2O$ is structurally similar to vivianite (Ito & Mori 1951) but H_2O-H_2O bonding is not as important in the former. Interestingly, we see from Figure 2 that "Δ_{VI}" for Fe^{2+} in its rather distorted sites in ludlamite is low, but not to the same extent as the value for vivianite. Crystal-field weakening processes, however, must also be important in the structure of ludlamite. The spectrum of ludlamite is shown in Fig. 6.

Conclusions

Although they are not universally applicable or capable of leading to unequivocal solutions, the "reference curves" in Fig. 2 and 3 have potential value in facilitating the interpretation of the electronic absorption spectra of many Fe^{2+}-bearing materials in the following ways :

(a) establishing the validity of band assignments and permitting a distinction between "*d-d*" and *M-M* charge-transfer bands (*e.g.*, tourmaline, cordierite, osumilite, corundum) ;

(b) indicating the possible presence of hidden weak "*d-d*" bands (*e.g.*, osumilite, corundum) ;

(c) indicating peculiarities in bonding of Fe^{2+} in certain structures (*e.g.* vivianite, ludlamite) ;

(d) estimating the approximate average *M*-O bond distance of materials whose structures are unknown.

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