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

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Faye suggests that the band around 16000 cm^{-1} in iron-containing corundum arises from an intervalence transition between adjacent ions of Fe^{2+} and Fe^{3+}, while we attribute it to a split component of the $^5T_2 \rightarrow {}^5E$ ligand field transition, the splitting being due to the strong Jahn-Teller effect acting on the E state in octahedral symmetry.

The following points may demonstrate that none of the arguments presented by Faye contradicts our interpretation which, in contrast to his suggestion, does not require any special assumptions that are not supported by the experimental results.

1. Jahn-Teller splittings between 4000 and 4800 cm^{-1} are reported for the $^5T_2 \rightarrow {}^5E$ transition of Fe^{2+} in $MgTiO_3$, Zn_2TiO_4, Zn_2SnO_4, $MgAl_2O_4$, $MgGa_2O_4$, and $MnGa_2O_4$, with Fe^{2+} substituting for ions in octahedral coordination (Brokopf, Reinen, and Schmitz-Dumont, 1970). These splittings are in the same range as those of 5000 and 4600 cm^{-1} proposed for Fe^{2+} in corundum, showing that our interpretation is reasonable.

2. The average value of 10 Dq in these compounds is 11450 cm^{-1}, even higher than that of 10800 cm^{-1} for Fe^{2+} in MgO taken to be typical for Fe^{2+} in an octahedral site of normal size. For sites of lower than cubic symmetry 10 Dq is always lower than the band position due to the splitting of the T_2 ground state. For Fe^{2+} in corundum, this splitting was estimated to be 900 cm^{-1} in analogy to Ti^{3+} in corundum (McClure, 1962). This results in a Dq value of 1080 cm^{-1} for Fe^{2+} in corundum if only the band at 11400 cm^{-1} is interpreted as a ligand field band. For σ-polarization, this band has an almost perfectly Gaussian shape. The halfwidth on the high energy side is 8 percent higher than on the low energy side, that is, within the normal range for a single band (Jørgensen, 1962, p. 93). These observations do not support the suggestion of a second band on the high energy side of the maximum. For the π-spectrum the experimental errors are too large to allow reliable conclusions. This second band would have to be at or above 14000 cm^{-1} to give reasonable Dq values. Without experimental evidence for this "hidden" band, the interpretation of Faye results in too low Dq values for Fe^{2+} in corundum while Dq values near 1330 cm^{-1} as given in our paper are in agreement with the well established $Dq \alpha R^{-5}$ dependence.

3. For spin-allowed ligand field bands at room temperature the normal halfwidth (bandwidth at half height of maximum absorbance) is around 3000 cm^{-1} (Jørgensen, 1962, p. 93). The somewhat larger halfwidths found for the absorption bands of Fe^{2+} in corundum might be due to the variation in the metal-oxygen bond distances in the corundum lattice (Newnham and de Haan, 1962).

4. As pointed out in our paper the band polarizations observed are to be expected if the $^5A_1$ component of the $^5T_2$ ground state lies lowest. The metal-metal vector along the c axis shares three octahedral edges in contrast to only one for each of the three vectors perpendicular to c. Therefore we would expect the dichroism of an intervalence band to be smaller than observed for the band around 16000 cm^{-1}. Thus the observed dichroism is consistent with our interpretation.

Clearly more experimental evidence is needed to decide between the two alternatives. If the bands at 11400 and around 16000 cm^{-1} were of different origin, their relative heights should vary in different crystals. The height of a ligand field band of Fe^{2+} is proportional to the concentration of Fe^{2+} while the height of an intervalence transition should vary with the concentration of Fe^{2+}–Fe^{3+} pairs, *i.e.*, with the product of the concentrations of both Fe^{2+} and Fe^{3+}, and should be completely absent in a crystal containing only divalent iron. We did observe a nearly constant ratio of the two bands in all crystals studied with the Fe^{2+}/Fe^{3+} ratio varying by about a factor of ten. This clearly favors our interpretation. Due to the uncertainty in the analyses, the extensive overlap of bands and the presence of varying amounts of other transition metal impurities with absorption bands in this region, however, our results are not fully conclusive, and a more systematic investigation of this point is called for.

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