American Mineralogist, Volume 59, pages 630–631, 1974

The Polarized Spectra of Iron in Silicates: II. Olivine: A Reply

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The discussion paper by Burns (1974) highlights the need for a full understanding of the contributions by both *M*(1) and *M*(2) sites to the olivine spectrum. Runciman, Sengupta, and Gourley (1973) attempted to explain the major features in terms of the *M*(2) sites. In particular, a detailed crystal field model was proposed and relative polarization intensities calculated. It was recognized that we had not explained all the features of the spectrum, but it was felt that a significant contribution to the interpretation of the olivine spectrum had been made.

The arguments put forward by Burns (1974) are persuasive. It seems that the remaining features in the near infrared spectrum of olivine are due to ions on the *M*(1) site. It should be noted that we never rejected this possibility in our paper, but examined whether vibronic coupling could be responsible for such a high intensity in a centrosymmetric $d \rightarrow d$ transition.

In the earlier paper we claimed that the olivine bands were temperature independent and hence there could not be any strong vibronic coupling. These conclusions were based on the study of the γ spectrum of our sample, which was the only polarization whose temperature dependence could be accurately tested. We have recently repeated the experiment for the α, β, and γ near infrared spectra of another sample. Figure 1 shows that the total intensity of the γ spectrum, dominated by the intensity of the band at 9540 cm^{-1}, changes little in going from 19 K to room temperature while each of the total intensities of the α and β spectra, dominated by the intensities of side bands, increases by about 50 percent. This indicates vibronic coupling of the side bands and is consistent with assigning them to the *M*(1) site.

In Table 1 (Burns, 1974), a comparison of intensities for different iron complexes is presented. The $d \rightarrow d$ transition intensities strongly depend on the positions and symmetries of higher odd states and the coupling mechanism between odd and even states. These are in turn determined by the coordination of the complex and the types of ligands present. Therefore, the comparison of intensities should be confined to the octahedral silicate minerals, enstatite, olivine, and cummingtonite.

Burns proposes that the intensity of the band due to the non-centrosymmetric site in olivine is too low compared to other silicates, and not that the intensity due to the centrosymmetric site is too high. This is a possibility, as sites with higher distortion give more intense bands. Accordingly, cummingtonite with a severely distorted site has more intense bands than olivine and enstatite, as expected.

Some of the points made by Burns in his concluding remarks need clarification. We feel that the dominant band in the γ spectrum in the near infrared and some features in the far infrared spectra due to Fe^{2+} have been adequately explained by our model. Two different electronic transitions at the *M*(2) site contribute to absorption in the region described by Burns as band II. This means that there are four bands to be explained in this region, and not three as suggested by the nomenclature of Burns. The model did not predict any absolute value of extinction coefficient, and therefore we cannot see how the success of the model can be assessed from Table 1 of Burns. The present discussion treats the assignment of remaining features in terms of the *M*(1) site, and this in no way interferes with the interpretation of the *M*(2) site as implied by Burns.

The principle that centrosymmetric sites have an order of magnitude lower transition probability is not a "rule of thumb," but is based on sound quantum mechanical and symmetry arguments. The centrosymmetric sites do give bands of appreciable intensity in solids, not because the principle is wrong, but because in solids there can be strong vibronic coupling, covalency, and charge transfer effects. In fact Burns mentions these possibilities when he talks about interaction with next-nearest neighbors.

In conclusion we agree that Burns' arguments and our recent results have clearly demonstrated that the extra bands in the near infrared spectrum of olivine are due to iron ions on the *M*(1) site. However, the exact mechanism and the theory involved remain to

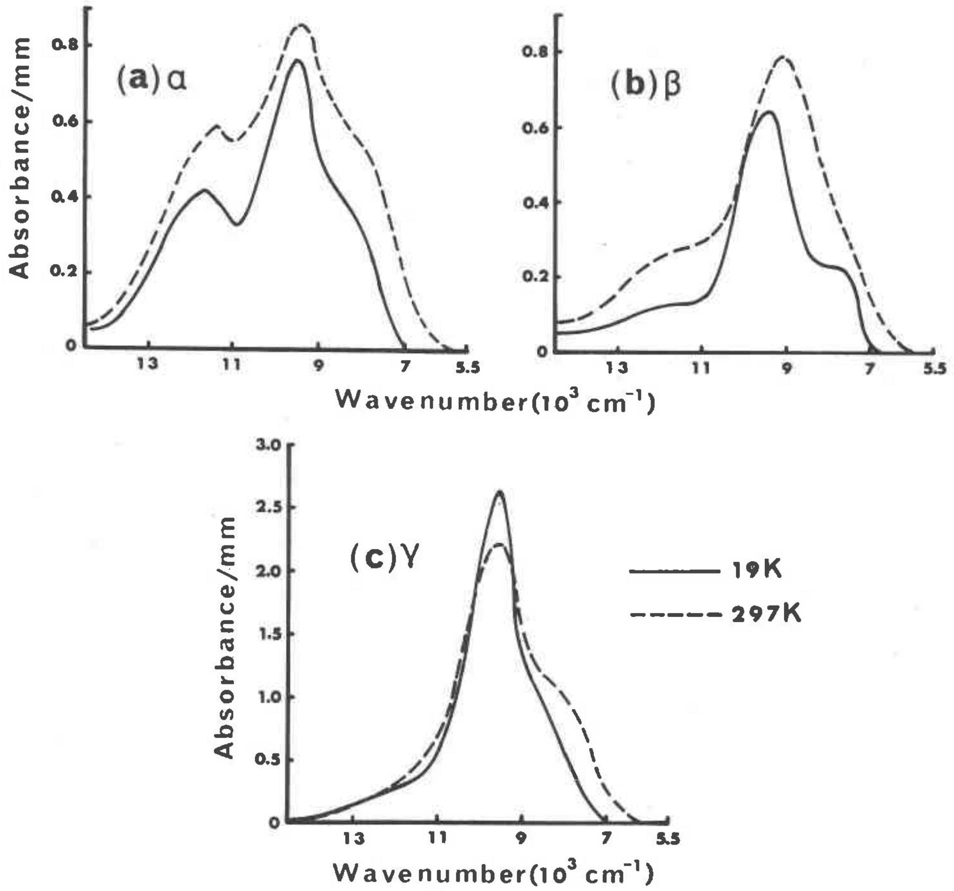

FIG. 1. Polarized spectra of olivine in the range 5500–14500 cm^{-1} at 19 K (solid line) and 297 K (dashed line). (a) α spectrum; (b) β spectrum; (c) γ spectrum.

be established. A crystal field analysis consistent with the crystallographic data of the $M(1)$ site should be attempted. An extra infrared band of the olivine spectrum (1780 cm^{-1}, β polarized) has been observed (Runciman, Sengupta, and Gourley, 1973). The monticellite spectrum should be extended to this region to clarify whether this band is also due to the $M(1)$ site.

References

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Manuscript received, October 9, 1973; accepted for publication, February 5, 1974.