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Crystal-structure refinement and optical properties of a Ti^{3+} fassaite from the Allende meteorite: Reply[1]

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Abstract

Arguments advanced by Burns and Huggins in favor of the splitting of the octahedral crystal-field absorption of Ti^{3+} may be correct, but if so, need have no effect on the assignment of a strong band at 16,500 cm^{-1} in the spectrum of the Allende fassaite to Ti^{3+}–Ti^{4+} charge transfer. The polarization of this absorption demonstrates that it is not primarily a crystal-field absorption. A relatively weak crystal-field absorption of Ti^{3+} is evidently present at 21,000 cm^{-1} in the spectrum of the Allende fassaite; if a lower-energy component is also present, it should have comparable intensity and would probably be obscured beneath the Ti^{3+}–Ti^{4+} charge-transfer band.

If a pronounced splitting of the Ti^{3+} crystal-field absorption does exist in pyroxenes, this constitutes an argument against previous assignments by others of a single band at 18-22,000 cm^{-1} in the spectra of terrestrial titanaugites to Ti^{3+}, since a low-energy (~16,500 cm^{-1}) component has not been detected.

Introduction

The major part of Burns and Huggins' discussion is concerned with a topic, the splitting of the octahedral crystal-field absorption of Ti^{3+}, which we are not inclined to dispute at this time, but which we consider is not a direct refutation of our principal assignments. Nor do we consider their Ti^{3+} crystal-field assignment of the 16,500 cm^{-1} band in the Allende pyroxene to be a valid alternative to our Ti^{3+}–Ti^{4+} charge-transfer assignment; Burns and Huggins seem to ignore the observations which rule out their assignment.

Observations against the Crystal-field Hypothesis

Our measurements indicate that the 16,500 cm^{-1} absorption band is strong only for light with a component of electric vibration in (100). As explained in some detail in our paper, this is perfectly compatible with charge-transfer. However, it is not a plausible polarization for a crystal-field absorption. Our original discussion of this point was incorrect; such a polarization might be explained on the basis of a crystal-field absorption if the $M1$ site had effective axial symmetry with axis perpendicular to (100). One of the pseudo-three fold axes of the $M1$ octahedron is, in fact, approximately perpendicular to (100). However, the octahedron is not distorted in such a way as to yield three-fold symmetry on this axis with other symmetry destroyed, and furthermore the structure exclusive of the $M1$ octahedron is not at all close to three-fold symmetry with respect to this axis. Therefore, there remains no reason to expect a crystal-field absorption to be polarized with respect to (100). Burns and Huggins have not shown how our reasoning could be faulty in interpretation of the observations, nor have they presented any observations of their own which conflict with ours.

In addition to the direct observations of the pleochroism, our measurement and analysis of the dispersion also suggest that the 16,500 cm^{-1} band is strongly polarized in (100). Again, Burns and Huggins present no explanation whatsoever for the inclined dispersion.

In the absence of valid arguments which specifically rule out our Ti^{3+}–Ti^{4+} charge-transfer assign-

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ment of the 16,500 cm^{-1} band (see below), these observations clearly establish our hypothesis as preferable.

Arguments against the Charge-transfer Hypothesis

The lengthy arguments by Burns and Huggins concerning the expected splitting of the Ti^{3+} crystal-field absorption, even if correct, probably have no bearing on our assignment of the 16,500 cm^{-1} band to Ti^{3+}–Ti^{4+} charge transfer. If the crystal-field absorption of Ti^{3+} is actually split, we would expect the two components to have roughly comparable intensities. The band at 21,000 cm^{-1} which we assigned to Ti^{3+} is weak relative to the 16,500 cm^{-1} band; hence the low-frequency component should also be relatively weak, and if it occurs at about 16,500 cm^{-1} as suggested by Burns and Huggins, it would be effectively masked by the much stronger Ti^{3+}–Ti^{4+} charge-transfer band. There is no reason why both types of absorption could not occur at about the same location; however, the polarization of the 16,500 cm^{-1} band and its greater intensity relative to the 21,000 cm^{-1} band indicate that most of the absorption at this location is caused by charge-transfer.

The only arguments by Burns and Huggins which could, if correct, rule out our assignment, are given in their section (f). However, we do not consider either of these to be at all well-founded. First, they give polarized absorption spectra for the *X*, *Y* and *Z* optical direction of a hedenbergite, pointing out that the intensity of the Fe^{2+}–Fe^{3+} charge-transfer band does not show large variation in these spectra. They claim this proves that *M* site charge-transfer bands are not strongly polarized; however, their citation of these data merely shows that they misunderstand the proposed mechanisms and geometry of the *M* site charge transfer. The relative intensities of the proposed type of charge transfer absorption in various electric vibration directions should be given, to a first approximation, by the square of the projection of unit vectors in these directions onto the metal-metal vector. In hedenbergite, the *X* and *Z* optical directions are at angles of near 45° to the plane (100). If the absorption is polarized in (100), these directions, because they are at equal angles with (100), should have approximately the same absorption intensity. As for optic direction *Y*, we perform a simple trigonometric analysis, using the 45° angle between *X* or *Z* and *c*, and the angle in (100) of about 60° between the *M*1–*M*1 vector and *Y*. This yields an expected intensity ratio, $X:Y:Z$, of approximately $1:2/3:1$ for pure *M*1–*M*1 transfer. If *M*2–*M*1 transfer is also involved, the absorption in *Y* would be augmented. Thus, for the *X*, *Y* and *Z* directions reported by Burns and Huggins, we predict approximately equal intensity, as observed.

Second, Burns and Huggins claim that the relative intensities of the 21,000 and 16,500 cm^{-1} bands are not consistent with our assignments. On the contrary, our observations indicate that the 16,500 cm^{-1} band is much stronger than the 21,000 cm^{-1} band (as shown in our Figure 1a) and hence, an assignment of both bands to crystal-field transitions of Ti^{3+} is unlikely. Again, Burns and Huggins' interpretation would depend on observations conflicting with our own, but none have been provided.

Conclusion

In lieu of data or arguments which could contradict our assignments, Burns and Huggins seem to have substituted a prejudice in favor of crystal-field interpretations. Their arguments in favor of splitting of the crystal-field absorption of Ti^{3+} are interesting; however, if they are correct, it would mean not that our assignments of the Allende pyroxene spectra are invalid or unlikely, but that previous assignments (Chesnokov, 1959; Manning and Nickel, 1969; Burns, 1970) of a single absorption band at 18–22,000 cm^{-1} in the spectra of terrestrial titanian pyroxenes should be suspected. We note with interest that Burns *et al* (1972) have recently attempted to modify assignments in terrestrial titanian augites, abandoning the Ti^{3+} assignment of the 18–22,000 cm^{-1} band. They proposed instead an assignment of this band to spin-forbidden transitions of Fe^{3+} in tetrahedral coordination. However, this must be regarded as unlikely in view of the extreme weakness of spin-forbidden absorptions in relation to charge-transfer absorptions, and the fact that this assignment does not account satisfactorily for the strong pleochroism of terrestrial titanaugites. We would like to point out once again that our suggested assignment of the 18–22,000 cm^{-1} band in terrestrial and lunar pyroxenes to Fe^{2+}–Ti^{4+} charge-transfer, and our assignment of the 16,500 cm^{-1} band in the Allende pyroxene (and possibly a similar band in the spectra of lunar augites) to Ti^{3+}–Ti^{4+} charge-transfer, account very well for the relative intensities of these bands on the basis of the expected amounts of Fe^{2+},

Ti^{3+} and Ti^{4+} ions present. (We expect no Ti^{3+} in terrestrial pyroxenes, but possibly a minor amount in lunar pyroxenes).

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