

On the Color Centers of Iron in Amethyst and Synthetic Quartz: A Discussion

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Two recent papers published by Cohen and Hassan (1974) in this journal present results of optical absorption, biaxiality, optical and thermal bleaching studies. The conclusions drawn from their results about the structures of the various centers involved completely neglect recent results obtained by a number of authors (Matarrese, Wells, and Peterson, 1969; Dennen and Puckett, 1972; Lehmann, 1967, 1970, 1971; Lehmann and Bambauer, 1973). Well established results of electron paramagnetic measurements (EPR) and ligand field interpretations of optical spectra are either termed unlikely or not considered (and cited) at all. As a result the proposed models partly contradict these results (coordination and site occupation of Fe^{3+} and Fe^{2+}) and partly do not (at least in our view) represent physically meaningful pictures (proposed structures of amethyst color centers). While the results presented by Cohen and Hassan support the models based on these EPR and optical data (Lehmann and Bambauer, 1973), the conclusions drawn disturb rather than clarify the picture. Although it is not possible to repeat all the evidence in detail (which the reader will be able to extract from the above cited literature himself), we want to stress the following points:

(1) Cohen and Hassan attribute the intense band at about 5.6 eV or 46000 cm^{-1} present in amethyst and under the rhombohedral faces in synthetic iron-doped quartz to Fe^{3+} in interstitial sites of approximately octahedral symmetry. Comparative studies of optical spectra of Fe^{3+} with oxygen ions as nearest neighbors (Lehmann, 1970) clearly established that octahedral symmetry places the first charge transfer band of Fe^{3+} at or below 41000 cm^{-1} or 5.1 eV (decreasing with distortion from the ideal O_h symmetry). On the other hand Fe^{3+} in tetrahedral lattice sites of both AlPO_4 and GaPO_4 shows a charge transfer band at 46000 cm^{-1} or 5.6 eV. Thus the band at this position in quartz must be due to Fe^{3+} on lattice sites (S centers). This conclusion is in complete agreement with EPR work of Barry, McNamara, and Moore (1965) and with earlier findings of Tsinober

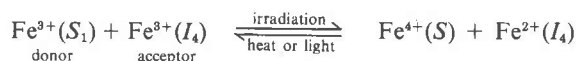
and Chentsova (1959), both cited but misinterpreted by Hassan and Cohen with respect to the site occupation of Fe^{3+} .

(2) The absorption spectrum of Fe^{2+} in green portions of synthetic quartz *proves* (not merely suggests) this ion to occupy interstitial sites of distorted octahedral symmetry (I_6): The bands at 10100 and 13800 cm^{-1} are due to the ${}^5T_2 \rightarrow {}^5E$ transition split by the lower symmetry (Lehmann, 1967). Cohen and Hassan take a similar band present in this region in amethyst as evidence for the presence of such a center in amethyst. However, there are marked differences in position, shape, and dichroism of the two band systems, and for an identical center the ligand field spectrum must also be identical, not just similar. A detailed ligand field interpretation assigns the band in amethyst to the ${}^5T_2 \rightarrow {}^5E$ transition of Fe^{4+} on silicon sites (Lehmann, 1967).

(3) Contrary to the statement of Hassan and Cohen the band at about 6.2 eV or 51000 cm^{-1} has been found earlier in synthetic, iron-doped quartz together with a shoulder near 41000 cm^{-1} (Lehmann, 1970). The position of the first band as well as the weaker ligand field spectrum are consistent only with Fe^{3+} in interstitial sites of distorted tetrahedral symmetry (I_4). While the EPR spectrum of this center would also be consistent with a substitutional Fe^{3+} without short range charge compensation (Matarrese *et al.*, 1969), this assignment has been confirmed by the charge transfer spectra of Fe^{3+} in alkali silicate glasses (Lehmann and Steinmann, to be published). The assignments to substitutional and interstitial centers given by Cohen and Hassan for the bands at 6.2 and 5.6 eV are seen to be reversed from the ones established by correlation of optical spectra and predictions of ligand field theory.

(4) The EPR work of Barry *et al.* (1965) clearly established substitutional Fe^{3+} (S_1 centers) as a precursor of the amethyst color center. This was confirmed in later EPR work and in addition it was found that interstitial Fe^{3+} (I_4 centers) also acts as a precursor in natural and synthetic amethyst, both centers being

necessary for the generation of amethyst color centers (Lehmann and Moore, 1966). The maximum concentration of amethyst color centers produced by irradiation is limited by the center present in smaller concentration. This fact is consistent only with a model in which one of them acts as the donor, the other one as the acceptor of the transferred electron:



(The reverse process with S_1 centers as acceptors and I_4 centers as donors would be extremely unlikely as a result of ionizing irradiation).

This model is in complete agreement with the predictions of ligand field theory. The visible coloration of amethyst is dominated by Fe^{4+} whereas Fe^{2+} just contributes a weak band near 6000 cm^{-1} and a charge transfer band above 50000 cm^{-1} (Lehmann, 1967). This model is (except for the coordination of the interstitial ion) practically equivalent to the one proposed by Cohen and Hassan. However, in contrast to the smoky quartz center and other color centers associated with main group metal ions, a hole associated with a transition metal ion is (at least in its electronic ground state) highly localized on this transition metal ion. Therefore the only reasonable physical description for centers of this kind seems to us to be one with the valency increased by one for the electron donor and decreased by one for a transition metal ion as electron acceptor. The existence of these ions then must result in ligand field and charge transfer spectra specific for both valency and coordination of these ions. The positions and intensities of absorption bands are predictable within rather narrow limits, but do not necessarily bear any resemblance to those of hole or electron centers associated with main group ions as implied by Schlesinger and Cohen (1966) in an earlier publication.

The occurrence of amethysts that rapidly bleach in daylight (H. Harder, private communication) indicates that other defects besides interstitial Fe^{3+} may act as electron acceptors in amethyst.

(5) The work of Barry *et al* (1965) clearly demonstrated the optical biaxiality of amethyst to be caused by the unequal substitution of the three lattice sites by Fe^{3+} (and furnished an explanation for the different degree of biaxiality in different crystals). The thermal equilibration among these sites at temperatures near 600°C has also been established by these authors and was confirmed in later work. This equilibration as well as the changes in the EPR spectra

accompanying the precipitation of Fe_2O_3 particles that occurs in highly colored amethysts in the same temperature range (Lehmann, 1971) prove migration of substitutional Fe^{3+} . We agree with Cohen and Hassan that this result is highly surprising for a trivalent ion bound by partly covalent $M\text{-O}$ bonds, but nevertheless it has to be accepted as an experimentally proven fact. If the equilibration occurs *via* jumps from one lattice site to a neighboring one, each single diffusion jump will result in a net change of the occupation ratio of the three sites. In this way diffusion coefficients as small as $10^{-18} \text{ cm}^2/\text{sec}$ are sufficient to accomplish an equilibration. If, however, the equilibration occurs *via* preferential conversion of Fe^{3+} from the more highly substituted sites (*i.e.*, by an overall decrease of the S_1 center concentration), longer diffusion paths and consequently larger diffusion coefficients are necessary.¹ We are at present investigating these processes to determine the relative importance of these two mechanisms. In any case the brown particles of Fe_2O_3 are formed mainly from substitutional Fe^{3+} , not from interstitial ions alone as postulated by Cohen and Hassan, in amethyst.

In conclusion we may say that the method of electron paramagnetic resonance (EPR) gave final answers for a number of very specific problems. In contrast, ligand field theory can only serve to decide whether a model is consistent with the optical spectrum, but cannot definitely exclude additional models that were not specifically considered. However, in combination with the results of EPR, it places our model far beyond the mere likelihood of one among several equally plausible alternatives. This model has been completely confirmed in a recent investigation of natural amethysts from different locations (H. D. Stock and G. Lehmann, to be published).

¹ Note added in proof: Recent results (H. D. Stock and G. Lehmann, to be published) show the second mechanism to dominate.

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