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$^{2+}$ 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$^{2+}$ 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 ($I_a$): The bands at 10100 and 13800 cm$^{-1}$ are due to the $^4T_2 \rightarrow ^6E$ 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 $^4T_2 \rightarrow ^6E$ transition of Fe$^{3+}$ 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 ($I_a$). 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$^{3+}$ ($I_a$ 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 concentra-
tion 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:

$$\text{Fe}^{3+}(S_1) + \text{Fe}^{3+}(I_1) \xrightarrow{\text{irradiation}} \text{Fe}^{3+}(S) + \text{Fe}^{2+}(I_4)$$

(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 colora-
tion of amethyst is dominated by $\text{Fe}^{3+}$ whereas $\text{Fe}^{2+}$
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 con-
trast 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 coordi-
nation of these ions. The positions and intensities
of absorption bands are predictable within rather
narrow limits, but do not necessarily bear any resem-
bance 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) indi-
cates that other defects besides interstitial $\text{Fe}^{3+}$ may
act as electron acceptors in amethyst.

(5) The work of Barry et al (1965) clearly demon-
strated the optical biaxiality of amethyst to be
caused by the unequal substitution of the three lattice
sites by $\text{Fe}^{3+}$ (and furnished an explanation for the
different degree of biaxiality in different crystals). The
thermal equilibration among these sites at tem-
peratures 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 $\text{Fe}_2\text{O}_3$ particles
that occurs in highly colored amethysts in the same
temperature range (Lehmann, 1971) prove migration
of substitutional $\text{Fe}^{3+}$. We agree with Cohen and
Hassan that this result is highly surprising for a
trivalent ion bound by partly covalent $M$-$O$ bonds,
but nevertheless it has to be accepted as an ex-
perimentally 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 $10^{-18}$ cm$^2$/sec are
sufficient to accomplish an equilibration. If, however,
the equilibration occurs via preferential conversion of $\text{Fe}^{3+}$ from the more highly substituted sites (i.e., by
an overall decrease of the $S_1$ center concentration),
larger diffusion paths and consequently larger diffu-
sion coefficients are necessary. We are at present in-
vestigating these processes to determine the relative
importance of these two mechanisms. In any case the
brown particles of $\text{Fe}_2\text{O}_3$ are formed mainly from
substitutional $\text{Fe}^{3+}$, not from interstitial ions alone as
postulated by Cohen and Hassan, in amethyst.

In conclusion we may say that the method of elec-
tron 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 spec-
trum, 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).

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

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