

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

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The criticism of Lehmann (1975) in the preceding paper as to the neglect of recent literature in the two papers of Cohen and Hassan (1974) might have been tempered if he had noticed that the manuscript was received on January 10, 1972. Indeed the papers were written during 1970 and 1971 with the authors in two widely separated countries. The actual work was contemporaneous with an earlier paper published in *Science* (Cohen and Hassan, 1970). I am happy, however, that our results support the work of Lehmann and Bambauer (1973).

It might be mentioned here that my published work on color centers in smoky or amethyst quartz consists of some fifteen papers dating from 1954, the first paper on amethyst being in 1956. Lehmann's papers until now have neglected to reference any of this work, even though all but four of the papers are prior to his publishing in this field of research.

In answer to Lehmann's specific criticisms (the numbers refer to Lehmann's):

(1) "The intense band at about 5.6 eV" is not a simple band but consists of a complex band found only in rhombohedral growth in both natural and synthetic quartz. On the side of caution in our assignment of  $\text{Fe}^{3+}$  to a given site, we stated "that  $\text{Fe}^{3+}$  ion preferentially enters the  $\alpha$ -quartz structure in the positive rhombohedral growth regions and mainly interstitially (in a distorted octahedral environment)." The production of small brown microscopic particles on heating at 500°C strengthens the conclusion that the iron is interstitial and not substitutional (Cohen and Hassan, 1974).

(2) Lehmann uses the words "merely suggests" for our heading "Probable Nature of Center" in Table 2 (Cohen and Hassan, 1974). The term "probable" according to Webster: "Supported by evidence strong enough to establish presumption, but not proof". Thus we are again more cautious than Lehmann who states that the spectrum proves that  $\text{Fe}^{2+}$  occupies an interstitial site. If the  $\text{Fe}^{2+}$  is indeed proven to be in an interstitial site, then the  $\beta$ (5.6eV) bands are indeed due to interstitial  $\text{Fe}^{3+}$  as this interstitial  $\text{Fe}^{2+}$  band

grows upon the fading of the  $\beta$  bands as mentioned in the aforementioned Table 2. However, if Lehmann considers the  $\text{Fe}^{3+}$  to be so labile in the quartz structure that it can switch from substitutional to interstitial sites and precipitate on heating at 500°C, then it is difficult for us to have a meaningful discussion. If this were true then cation vacancies would be produced in quartz at relatively low temperature. This is counter to the evidence found for  $\text{Al}^{3+}$  in the substitutional site (Cohen, 1960). The substitutional  $\text{Al}^{3+}$  color center can be regenerated even after heating the quartz through the  $\alpha \rightarrow \beta$  transition and then cooling, only the interstitial  $\text{Al}^{3+}$  in the quartz being precipitated in the process.

(3) Lehmann bases interstitial tetrahedral symmetry of  $\text{Fe}^{3+}$  on the absence of ligand field bands in the infrared region. These would be difficult to detect with the total iron content at 120 ppm or below (Lehmann, 1971) as shown in his analyses. Total iron in our samples were all well below 100 ppm/wt. Lehmann states "that these band positions would be compatible with octahedral coordination of this ion, but this possibility has already been excluded by the absence of ligand field bands in the red part of the spectrum."

(4) For Lehmann's model to be correct, one must accept that holes cannot be stable near trace iron, thus  $\text{Fe}^{3+} + \text{hole} \rightarrow \text{Fe}^{4+}$ . Considering the stability of the  $\text{Fe}^{3+}$  half-filled  $3d$  shell and the unstable nature of the  $3d^4$  state, it is hard to accept that  $\text{Fe}^{3+}$  cannot have a stable hole on an adjoining oxygen whereas  $\text{Al}^{3+}$  can. However, it should be noted that, in the absence of most other transition ion impurity,  $\text{Mn}^{3+}$  ( $3d^4$ ) can exist in spodumene (Cohen and Anania, in preparation) so it may be that trace  $\text{Fe}^{4+}$  exists in quartz. If this is the case, it would not be reasonable to accept the presence of  $\text{Fe}^{4+}$  bands in the  $\text{Fe}^{2+}$  region of the spectrum. The  $\text{Fe}^{4+}$  is similar to the model for the 5450Å ( $\theta$ , 18,350 $\text{cm}^{-1}$ ) band (Schlesinger and Cohen, 1966), and it is suggested that this band would more likely be related to  $\text{Fe}^{4+}$  than a band in the  $\text{Fe}^{2+}$  spin-allowed region.

(5) The major disagreement with Lehmann concerns the conclusions of Barry, McNamara, and Moore (1965). The present authors feel that the precipitation of  $\text{Fe}_2\text{O}_3$  on heating amethyst is proof of interstitial  $\text{Fe}^{3+}$ , not migration of the pinned substitutional  $\text{Fe}^{3+}$  at temperatures near  $600^\circ\text{C}$ . The migration of  $\text{Fe}^{3+}$  from substitutional sites at temperatures  $500$ – $600^\circ\text{C}$  is not only "highly surprising" as Lehmann states but also unbelievable.

Lehmann offers no proof for his statement that "brown particles of  $\text{Fe}_2\text{O}_3$  are formed from substitutional  $\text{Fe}^{3+}$ , not from interstitial ions as postulated by Cohen and Hassan, in amethyst." The thermal equilibrium found near  $600^\circ\text{C}$  ( $500^\circ\text{C}$  in our experiments) could best be explained by movement of interstitial ions related to the color centers, not substitutional ones. This requires no disruption of the  $\sim 50$  percent covalent Fe–O bonds but merely migration of cations in the voids.

In conclusion it has been my experience that the only way to precisely relate electron paramagnetic resonance spectra to absorption spectra is to make both measurements simultaneously on the same sample following short bursts of ionizing radiation to study growth of bands before possible consecutive reactions can take place to confuse the picture. A plot of the two types of absorption *versus* each other allows one to relate the paramagnetic resonance band

to the related optical absorption band. Unless one uses this method it is difficult to relate a given color center band to the specific model determined by EPR.

In order not to delay the reply to the criticism of Lehmann, I have written this reply without consultation with my co-author, F. Hassan.

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