American Mineralogist, Volume 60, pages 338–339, 1975

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

ALVIN J. COHEN

Department of Earth and Planetary Sciences, University of Pittsburgh,
Pittsburgh, Pennsylvania 15260

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 Fe^{3+} to a given site, we stated "that Fe^{3+} ion preferentially enters the α-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 Fe^{2+} occupies an interstitial site. If the Fe^{2+} is indeed proven to be in an interstitial site, then the β(5.6eV) bands are indeed due to interstitial Fe^{3+} as this interstitial Fe^{2+} band grows upon the fading of the β bands as mentioned in the aforementioned Table 2. However, if Lehmann considers the 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 Al^{3+} in the substitutional site (Cohen, 1960). The substitutional Al^{3+} color center can be regenerated even after heating the quartz through the $\alpha \rightarrow \beta$ transition and then cooling, only the interstitial Al^{3+} in the quartz being precipitated in the process.

(3) Lehmann bases interstitial tetrahedral symmetry of 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 $Fe^{3+} + \text{hole} \rightarrow Fe^{4+}$. Considering the stability of the Fe^{3+} half-filled $3d$ shell and the unstable nature of the $3d^4$ state, it is hard to accept that Fe^{3+} cannot have a stable hole on an adjoining oxygen whereas Al^{3+} can. However, it should be noted that, in the absence of most other transition ion impurity, Mn^{3+} ($3d^4$) can exist in spodumene (Cohen and Anania, in preparation) so it may be that trace Fe^{4+} exists in quartz. If this is the case, it would not be reasonable to accept the presence of Fe^{4+} bands in the Fe^{2+} region of the spectrum. The Fe^{4+} is similar to the model for the 5450Å (θ, 18,350cm^{-1}) band (Schlesinger and Cohen, 1966), and it is suggested that this band would more likely be related to Fe^{4+} than a band in the 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 Fe_2O_3 on heating amethyst is proof of interstitial Fe^{3+}, not migration of the pinned substitutional Fe^{3+} at temperatures near 600°C. The migration of Fe^{3+} from substitutional sites at temperatures 500–600°C is not only "highly surprising" as Lehmann states but also unbelievable.

Lehmann offers no proof for his statement that "brown particles of Fe_2O_3 are formed from substitutional Fe^{3+}, not from interstitial ions as postulated by Cohen and Hassan, in amethyst." The thermal equilibrium found near 600°C (500°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 ~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.

References

BARRY, T. I., P. MCNAMARA, AND W. G. MOORE (1965) Paramagnetic resonance and optical properties of amethyst. *J. Chem. Phys.* **42,** 2599–2606.

COHEN, A. J. (1960) Substitutional and interstitial aluminum impurity in quartz structure and color center interrelationships. *J. Phys. Chem. Solids,* **13,** 321–325.

——— , AND F. HASSAN (1970) Iron in synthetic quartz: Heat and radiation induced changes. *Science,* **167,** 176–177.

———, AND ——— (1974) Ferrous and ferric ions in synthetic α-quartz and natural amethyst. *Am. Mineral.* **59,** 719–728.

HASSAN, F., AND A. J. COHEN (1974) Biaxial color centers in amethyst quartz. *Am. Mineral.* **59,** 709–718.

LEHMANN, G. (1971) Yellow color centers in natural and synthetic quartz. *Phys. Kondens. Mater.* **13,** 297–306.

——— (1975) On the color centers of iron in amethyst and synthetic quartz. *Am. Mineral.* **60,** 335–337.

———, AND H. V. BAMBAUER (1973) Quartz crystals and their colors. *Angew. Chem.* **85,** 281–289.

SCHLESINGER, M., AND A. J. COHEN (1966) Postulated structures causing the optical color center bands in amethyst quartz. *J. Chem. Phys.* **44,** 3146–3148.

Manuscript received, October 22, 1974; accepted for publication, December 23, 1974.