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Iron pairs in beryl: New insights from electron paramagnetic resonance, synchrotron X-ray absorption spectroscopy, and ab initio calculations

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Abstract

Beryl's various coloring make it a sought-after and precious gemstone. Knowledge on the physical origin behind the various colorings is essential to differentiate artificial colorings from natural ones. The blue color of the variety aquamarine has been proposed to be due to charge transfer between adjacent Fe^{3+}-Fe^{2+} pairs on the Al site and its adjacent 6*g* interstitial position, respectively. The present work presents the first experimental confirmation of such an arrangement.

Single-crystal electron paramagnetic resonance (EPR) spectra of a light blue beryl (Springbok, South Africa), before, and after annealing at 800 °C, have been measured at temperatures from 25 to 295 K and reveal two Fe^{3+}-Fe^{3+} pairs related to an axial Fe^{3+} center at the effective g = ~2.00 as well as a subordinate rhombic Fe^{3+} center at g = ~4.28. Powder EPR spectra show that the intensity of the axial Fe^{3+} center increases after annealing from 400 to 800 °C but becomes constant after 800 °C, whereas the rhombic Fe^{3+} center is not affected by annealing. One Fe^{3+}-Fe^{3+} pair is the same as the one investigated previously by Edgar and Hutton (1982) and arises from Fe^{3+} ions at the two nearest Al sites along the **c** axis. The best-fit spin Hamiltonian parameters show that the second Fe^{3+}-Fe^{3+} pair is also oriented parallel to the **c** axis and has a separation of 2.4 Å, corresponding to Fe^{3+} ions at an Al site and its nearest 6*g* interstitial position. The increased intensities of both Fe^{3+}-Fe^{3+} pairs after annealing suggest their formation from Fe^{3+}-Fe^{2+} and Fe^{2+}-Fe^{2+} precursors. Modeling of synchrotron Fe *K*-edge X-ray absorption spectra measured on the sample annealed at 1000 °C also shows occupancies of Fe^{3+} at both the Al site and the 6*g* interstitial position. The assignment of the rhombic Fe^{3+} center to the Be site remains tentative.

Keywords: Beryl, annealing, EPR, synchrotron XAS, ab initio, Fe^{3+}-Fe^{3+} pairs, Fe^{3+}-Fe^{2+} IVCT