Characterization of temperature behaviour of Mn^{2+} in calcite by electron paramagnetic resonance (EPR)

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In this study we discuss the temperature behaviour of the Mn^{2+} EPR spectrum in a pure natural calcite sample. The experiments were performed on microcrystalline powders using a EPR spectrometer equipped with a heating system, in the temperature range 293 - 473 K. The spectra show significant T-dependent changes in the hyperfine and zero-field splitting features. A small change of the Zeeman anisotropy is also observed.
As the temperature increases, the hyperfine splitting of the Mn(II) spectrum shows a uniform decreasing trend and a slight decrease of zero-field splitting. Interestingly, the whole spectrum slightly shifts to lower magnetic field values at the higher temperatures, thus tracing a small but appreciable change also in the Zeeman interaction. A small axial distortion, i.e., the compression or expansion, of the coordination polyhedron causes a magnetic anisotropy in the otherwise isotropic $^6S_{5/2}$ ground state of d^5 Mn(II), mixing in it orbitally degenerate crystal field excited states, through spin–orbit interaction. This is at the origin of the complex spectrum structure (Montegrossi et al. 2006).
We compared the present data with the structural changes in the investigated temperature range (Antao et al. 2009). These authors, in fact, noticed a simultaneous increase of the c-axis and decrease of the a-axis with increasing temperature, indicating that the pseudo-octahedral Ca site is increasing both its volume and geometrical distortion. The present EPR data suggest that the Mn(II) site is also changing. The decrease of the hyperfine splitting traces, through the change of the Fermi contact constant, the diminished admixture of 4s excited state into the $3d^5$ fundamental levels: this can be ascribed only to longer Mn-O bond distances. Moreover, changes in the zero-field splitting as well as in the Zeeman splitting can be explained in terms of changes of the axial distortion, which, however, is predicted to be reduced with increasing temperature (as zero-field interaction should largely increase, with increasing site distortion). All changes were found to be fully reversible.
These data represent an interesting insight towards the definition of a quantitative spectroscopic standard, the EPR spectrum of Mn(II), to trace out-of-equilibrium evidences in calcite with geochemical, environmental, and archaeometrical purposes.

References:
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Montegrossi G., Di Benedetto F., Minissale A., Paladini M., Pardi L.A., Romanelli M., Romei F. (2006), Appl. Geochemistry, 21, 820-825.