substance: Ti_nO_{2n-1} (n ≥ 3)
property: EPR spectra and defects in Ti_3O_5, Ti_4O_7

Literature: [75H, 71R, 76H, 71H, 74H1, 74H2].

Ti_3O_5: Spectra on single crystals [72S], on powder samples [74H3]. Twinned single crystals gave 2 EPR signals with $g_x = 1.960$, $g_y = 1.973$, $g_z = 1.978(1)$. The *x* and *y* axes are in the *a*-*c* plane and the *x*-axis is 22.5º to the *a*-axis for one signal and – 22.5º for the other. Spin concentrations are estimated to be 10^{-4} $n(Ti^{3+})$. Powder EPR data show hyperfine coupling; they were interpreted on the basis of the crystal structure, and Fig. 1 shows a detail of the structure in the *a*-*c* plane. Strong Ti(1) – Ti(1) and weaker Ti(3) – Ti(3) bonds exist at low temperatures. [76H] estimates that the Ti(1) – Ti(1) pair has a trap energy of 0.24 eV, and Ti(3) – Ti(3) of ≈ 0.067 eV. EPR signal is then due to excitation of Ti(3) – Ti(3) pairs to the conduction band. The observed EPR signal intensity at 77 K can be rationalized on this approach. The effective symmetry at Ti(3) is D_{2h} and $e_g \rightarrow a_g + b_{3g}$; $t_{2g} \rightarrow a_g + b_{2g} + b_{1g}$. Analysis gives $(\nu/c)(b_{2g}) - (\nu/c)(a_g) = 3100$ cm^{-1}, $(\nu/c)(b_{1g}) - (\nu/c)(a_g) = 6300$ cm^{-1}, $(\nu/c)(b_{3g}) - (\nu/c)(a_g) = 26000$ cm^{-1}. The EPR signals in Ti_3O_5 and the Magnéli phases have also been ascribed to (Ti^{3+}–V_0–Ti^{4+}) defects; axial *g*-values have been listed for all oxides in [74H3]. From optical data [72P] a trigonal distortion of 5000 cm^{-1} was estimated, and spin-orbit coupling constants 79.3...93.0 cm^{-1} have been calculated (cf. free-ion value of 135 cm^{-1}).

Ti_4O_7: Spectra interpreted in terms of an isolated substitutional Ti^{3+} ion associated with a cation vacancy, see [76L].

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Fig. 1.

Ti_3O_5. Detail of structure in the *a*–*c* plane of the LT phase [74H3].