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PALLADIUM COMPOUNDS WITH +III OXIDATION STATE

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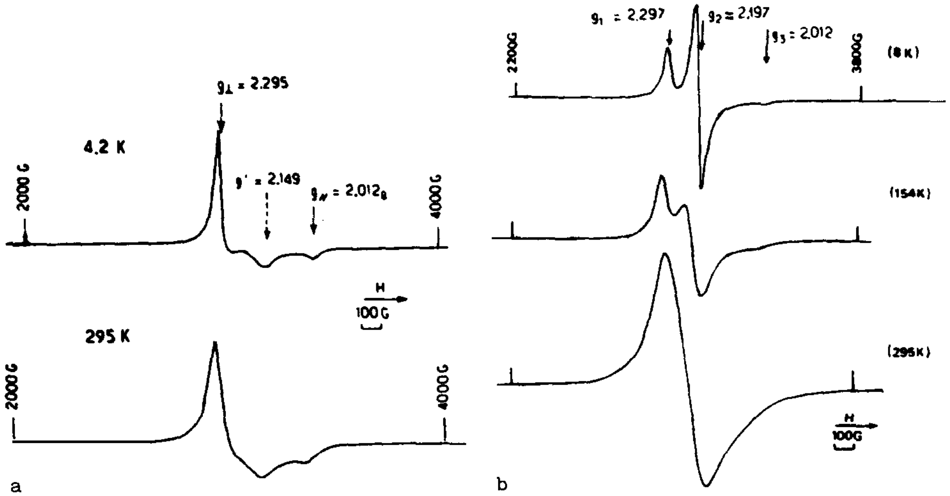
The trivalent oxidation state of palladium has been stabilized and unequivocally characterized in several fluoride series. $NaPdF_4$, whose structure can be derived from the $KBrF_4$ type, is obtained under high pressure and is quenched back to ambient conditions. Elpasolite compounds of A_2BPdF_6 formulation (A, B = alkali metal) are synthesized via solid state reactions.

Between 200 and 500 K every A_2BPdF_6 compound undergoes a tetragonal cubic phase transition.

The ESR spectra are characteristic of a doublet ground state. The $t_{2g}^6 e_g^1$ configuration of Pd(+III) is stabilized versus the $t_{2g}^5 e_g^2$ high-spin alternative by an important Jahn-Teller splitting of the ^2E_g state. In most cases ESR spectra are consistent with tetragonally elongated PdF_6 octahedra ; an orthorhombic component occurs for Cs_2KPdF_6 and Cs_2RbPdF_6.



ESR spectra with tetragonal (a-K_2NaPdF_6) and orthorhombic (b-Cs_2KPdF_6) symmetries.