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Note

Fluorine Magnetic Resonance Shifts in Paramagnetic PuF_4

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Plutonium tetrafluoride has so far not been investigated by NMR through such a study might yield additional information on the electronic structure of the fluorides of the actinide elements. PuF_4 which is isostructural with UF_4 , CeF_4 , ThF_4 , NpF_4 , HfF_4 , and ZrF_4 was prepared by hydrofluorination of plutonium dioxide at 600°C . The hydrogen fluoride had been previously treated with elemental fluorine and purified by subsequent distillations. The formation of plutonium trifluoride was prevented by a small addition of oxygen.¹

The ^{19}F NMR absorption was measured by a regenerative oscillator at a field of 9690 Gauss over the temperature range 30°C to -150°C . The observed PuF_4 powder absorption pattern is a many component one, see the Fig. 1.,

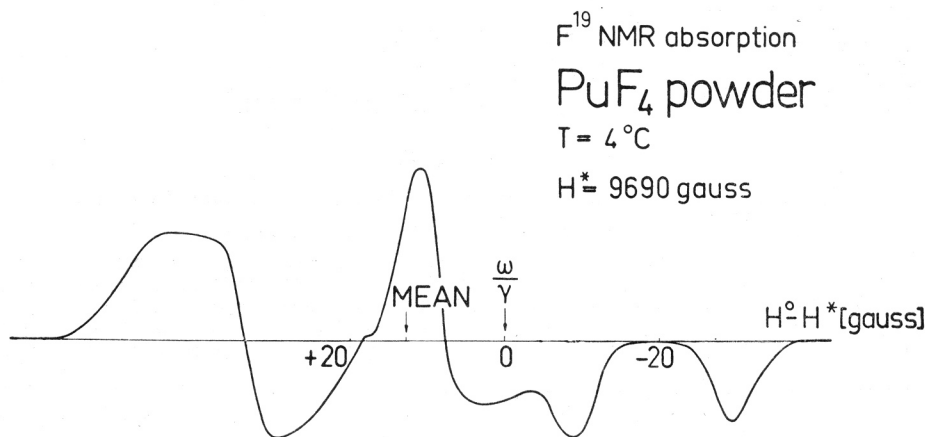


Fig. 1. The first derivative of the ^{19}F NMR absorption at 4°C and 9690 Gauss field. The bulk magnetization correction of 0.4 Gauss is not considered in the magnetic field scale.

and as there are seven nonequivalent fluorine sites in the unit cell² there is little change of making a direct assignment of the powder spectrum.

The spectrum has two maxima and could be graphically decomposed into two groups of components. The high field peak has its absorption maximum shifted some 0.3% up field compared with ω/γ , the other absorption maximum being shifted only slightly up field. The high field peak is quite symmetric, the low field group is asymmetric. The low field group is formed of at least two asymmetric component lines having their absorption mean shifted slightly

(0.06%) to low field. It should be mentioned that the low field group is quite similar to the many component ^{19}F absorption pattern of paramagnetic UF_4^3 .

The total absorption pattern median is shifted 0.11% up field at 30° C and 0.15% at -56° C; all shifts referring ω/γ . Over the temperature range 30° C to -56° C, $\Delta H/H$ is linear⁴ in $(T + 270)^{-1}$. Also the second moment is approximately linear in $(T + 270)^{-2}$ over this temperature range. Both linearities confirm the electronic paramagnetic origin of the ^{19}F NMR absorption asymmetry.

The observed resonance shift is assumed to be generated by combined contact and pseudocontact hyperfine interactions between fluorine nuclei and magnetic electrons. As is known, the origin of the shift could be explained and some evidence of partially covalent Pu-F bonds character obtained, providing the electronic g tensor was known. Unfortunately, no EPR data for the studied substances have so far been published.

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IZVLEČEK

Frekvenčni premiki magnetne resonančne fluorja v paramagnetnem PuF_4

Pri polju 9690 gaussov je bila z regenerativnim oscilatorjem izmerjena temperaturna odvisnost ^{19}F NMR absorpcije PuF_4 . Absorpcijski spekter sestoji iz dveh skupin absorpcijskih komponent. Obe skupini sta pomaknjeni k visokemu polju napram polju ω/γ , težišče spektra je pomaknjeno 0,15%. Odvisnosti pomika od temperature in od polja kaže, da ima pomik paramagnetni izvor in, da je posledica kontaktne in psevdokontaktne hiperfine interakcije med jedri ^{19}F in magnetnimi elektroni Pu iona.