

DISTORTION OF TcO_4 - ANION IN SOLID.

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Pertechnetate anion TcO_4 in aqueous and nonaqueous solution exhibits the regular tetrahedral T_d symmetry. According to theoretical data, a free TcO_4 anion has the same symmetry. In solid state, TcO_4 anion experiences distortions. Earlier [1,2], we have shown for a series of scheelite-like pertechnetates that Tc-99 quadrupole coupling constant (QCC) is strongly affected by the cation nature. Only two factors were assumed to influence the distortion of the pertechnetate anion: (i) anion site symmetry in the lattice and (ii) hydrogen or covalent bonding between an anion and a cation. In this paper, we report some regularities of the influence of the cation nature on the local electric field gradients (EFG) at the anion and the cation positions in the scheelite-like structures of the pertechnetates. For the most part, pertechnetates of monocharged cations crystallize into a scheelite-like (space group $I4_1/a$) or pseudoscheelite (space group $Pnma$) structure. The Tc atoms occupy special positions 4a, and the cations, placed in the cavities formed by the TcO_4 anions, occupy special positions 4b. CsTcO_4 undergoes a structural phase transition from $Pnma$ to $I4_1/a$ at high temperature. In order to decide between these alternatives, we studied the EFG dependences on unit cell volume V of the pertechnetates with uncharged cations: alkali metals, Ag, and NH_4 . The asymmetry parameters η of the EFG tensor at Tc-99 and cation nuclei are zero since the anions and cations are located on S_4 axis, and, therefore, axial symmetry of the EFG tensor should be realized. Thus, for the principal values of the Tc-99 EFG tensor, we may write

$$eq^{\text{exp}}(\text{Tc-99}) = (1 - \gamma) eq^{\text{lat}} + (1 - R) eq^{\text{val}} \quad (1)$$

(the zz subscript indices are omitted), where eq^{lat} is the lattice contribution and, eq^{val} is the valent contribution to the EFG. In the case of alkali-metal cations, it is usually assumed that $eq^{\text{val}} = 0$ and

$$eq^{\text{exp}}(\text{cation}) = (1 - \gamma) eq^{\text{lat}} \quad (2)$$

The lattice contributions are determined from the distances between the nuclei and the effective point charges or dipoles. Therefore, the linear dependences of eq^{lat} (Tc-99) and eq^{lat} (cation nuclei) on the reciprocal