Anomalous Temperature Dependence of the ^{99}Tc Quadrupole Coupling and Disordering of Cesium Positions in CsTcO$_4$

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A ^{99}Tc and ^{133}Cs solid-state NMR study of polycrystalline CsTcO$_4$ at a field of 7.04 T and temperatures from 90 to 430 K revealed first-order quadrupole effects. ^{99}Tc quadrupole coupling constant, C_Q, shows anomalous positive temperature coefficients and decreases from 2.0 MHz at 430 K to 0.45 MHz at 90 K. The asymmetry parameter, η (^{99}Tc), is zero at 430 K and 210 K. The high-temperature minimum of η is associated with a phase transition from orthorhombic to tetragonal and the second minimum reflects an orientational change of the principal axes q_{xx} and q_{yy} of the EFG-tensor.

The ^{133}Cs NMR spectra are characterised by a superposition of the two powder multiplets from the first-order couplings which arise from magnetically and crystallographically nonequivalent cesium sites, Cs (1) and Cs (2); the population ratio of Cs (2) and Cs (1), p_2/p_1, varies from 2.0 at 120 K to 6.5 at 373 K. The nonequivalence and population changes are attributed to the temperature change of the crystal field potential in the vicinity of the cations.

Key words: Technetium, Cesium, Solid State NMR, Quadrupole Effects, Phase Transitions.

Introduction

Cesium pertechnetate, CsTcO$_4$, crystallizes at room temperature in a orthorhombic form with the space group Pnma (D$_{2h}^{16}$); it forms a pseudoscheelite type lattice with the unit cell parameters $a = 5.726$, $b = 5.922$, and $c = 14.36$ Å [1, 2]. The TcO$_4^-$ anions and the Cs$^+$ cations occupy positions with local symmetry C_s [2]. ^{133}Cs NMR data for CsMnO$_4$ and CsReO$_4$, the structural analogs of cesium pertechnetate, have revealed magnetic nonequivalence of the Cs$^+$ cations [3].

According to DTA and X-ray data at (389 ± 5) K, CsTcO$_4$ experiences a first order phase transition from orthorhombic to a tetragonal form with the cell parameters $a = 5.898$, $c = 14.38$ Å, which is accompanied by the expansion of the cell volume [4].

The quadrupole coupling constant (QCC), C_Q, and the asymmetry parameter of the electric field gradient (EFG), η, for the ^{99}Tc nuclei in CsTcO$_4$ are direct indicators of the crystal symmetry since C_Q and η are depended on the electronic environment in the crystal. Earlier we have measured by ^{99}Tc solid-state NMR first order quadrupole effects in CsTcO$_4$ with C_Q and η equal to 1.25 (5) MHz and 0.22 (5), respectively, at 293 K [5]. The values obtained for the EFG and η are within the range of values expected for a packing-induced effect which dominates the temperature behaviour of the EFG-tensor.

We have shown that there is a linear dependence of $|e\,q_{zz}|$ on the reciprocal unit cell volume, V, for the alkali metal (Na, K, Rb) and ammonium pertechnetates with scheelite structure [5, 6]:

$$(e\,q)_{\text{exp}}(^{99}\text{Tc}) = a\,V^{-1} + b, \quad (a > 0). \quad (1)$$

This dependence gives evidence of the same signs of the valence (q_{val}) and lattice (q_{lat}) contributions to the ^{99}Tc EFG in the pertechnetates [6].

To clear specific features of the EFG in the cationic and anionic positions of CsTcO$_4$, the temperature dependences of the magnetic resonance parameters of the ^{99}Tc and ^{133}Cs nuclei will discussed.

Experimental

Cesium pertechnetate was synthesized by the interaction of CsNO$_3$ ND$_4$TcO$_4$ in aqueous solution. The
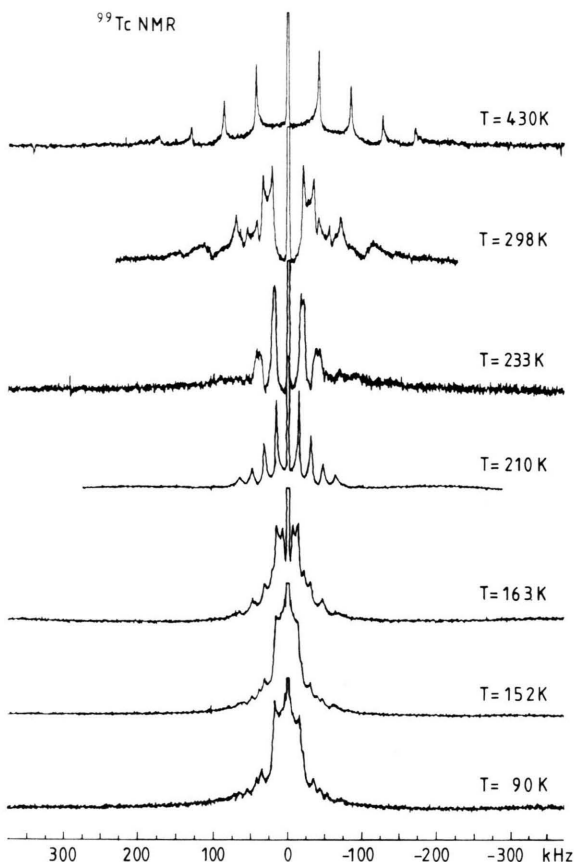
Fig. 1. ^{99}Tc NMR spectra (67.5 MHz) of polycrystalline $CsTcO_4$ with first order quadrupole splitting at different temperatures; sweep range: spectral width = 1 MHz; number of scans = 100.

Fig. 2. Temperature dependence of the ^{99}Tc QCC, $C_Q = e^2 q Q/h$, (○), asymmetry parameter, η (△), and chemical shifts, δ (◇) for ^{99}Tc NMR in $CsTcO_4$.

individuality of the compound was proved by chemical and X-ray phase analysis. The sample of $CsTcO_4$ was a white polycrystalline powder with a dispersity Φ 30–50 µm. DTA revealed a weak exothermal effect at 390 K.

The ^{99}Tc (67.5 MHz) and ^{133}Cs (39.8 MHz) NMR spectra have been recorded on a Bruker MSL-300 spectrometer at a field $B_0 = 7.04$ T in the temperature range 90–430 K. A one-pulse sequence with a variable dead time (5–7 µs) was used for the excitation of a spin system; the pulse width was 1 µs with 5 s delays.

The isotropic chemical shifts have been determined relative to resonances of aqueous solutions of CsBr (0.5 M) and NH_4TcO_4 (0.1 M). Temperature dependent experiments were carried out using a Bruker B-VT-1000 thermostat with a temperature tolerance $\Delta T \pm 1$ K.
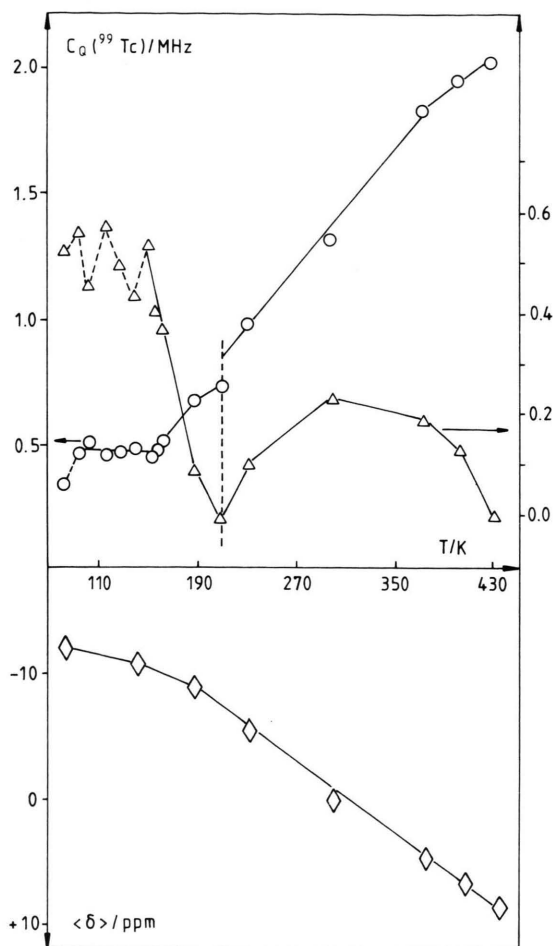
Results and Discussion

^{99}Tc NMR

Figure 1 shows the temperature dependence of the ^{99}Tc NMR line shape of $CsTcO_4$, which is dominated by first-order quadrupole effects. The spectra consist of nine lines, the satellites having a complicated shape due to a nonzero asymmetry parameter, η. The central component ($-1/2 \leftrightarrow 1/2$ transition) remains symmetrical even in the low-field experiments ($B_0 = 1.4$–2.1). Hence, second-order quadrupole coupling and chemical shift anisotropy seem to be negligible in the case of ^{99}Tc NMR for $CsTcO_4$. The chemical shift of the ^{99}Tc NMR varies insignificantly over the whole temperature range (from -10 to 10 ppm).

The first-order NMR powder pattern is characterized by three specific points on the frequency scale: v_{sg} (singularity), v_{sh} (shoulder) and v_{st} (step). Using the relations between v_Q, η, Δv_{sg}, Δv_{sh}, and Δv_{st} from [7], we have constructed a set of theoretical line shapes (histogram) for $I = 9/2$. The values of v_Q and η have been determined by comparison of the calculated and experimental spectra. The temperature dependences of C_Q and η for the ^{99}Tc nuclei are shown in Figure 2.

The $C_Q(^{99}\text{Tc})$ temperature dependence is anomalous with a positive temperature coefficient

$$\Delta C_Q/\Delta T \simeq 6\,\text{kHz} \cdot \text{K}^{-1}.$$

The asymmetry parameter, η, becomes zero at 210 K and at 430 K. The realization of axial symmetry of the ^{99}Tc EFG tensor at 430 K reflects the phase transition from orthorhombic to tetragonal. The value $C_Q = 2.0$ MHz at 430 K agrees with the value obtained by extrapolation of the linear dependence (1) for the pertechnetates with scheelite structure.

Since no phase transitions have been detected in the low temperature range, the zero value of η at 210 K seems to arise from a displacement of the ^{99}Tc EFG tensor axes. The ^{99}Tc EFG tensor components at different temperatures have been determined except for the sign, on assuming that the principal axes system remained unaltered for the whole temperature range measured, by

$$\sum_{i=x,y,z} q_{ii} = 0,$$

$$\eta = \left| \frac{q_{xx} - q_{yy}}{q_{zz}} \right|,$$

$$q_{zz} = \frac{h\,C_Q}{e\,Q\,(1-\gamma)}$$

$$= 0.4137\,\frac{C_Q(\text{MHz})}{Q(\text{barn})(1-\gamma)}\,[10^{20}\,\text{Vm}^{-2}],$$

$$Q = 0.5\,\text{barn}, \quad (1-\gamma) = 6.$$

(2)

Figure 3 shows that the $q_{xx}(T)$ and $q_{yy}(T)$ curves cross at 210 K. Hence, the break in $\eta(T)$ at 210 K is a result of the reversing of the submodule difference sign in (2). Slight oscillations of $\eta(T)$ below 150 K (Fig. 2) seem to be a result of the variation of the $q_{ij}(^{99}\text{Tc})$ absolute values due to the charge redistribution on the oxygen and technetium atoms in the TcO$_4^-$-anion [5].

The reported results have shown that in the case of CsTcO$_4$ the absolute values of the ^{99}Tc EFG tensor
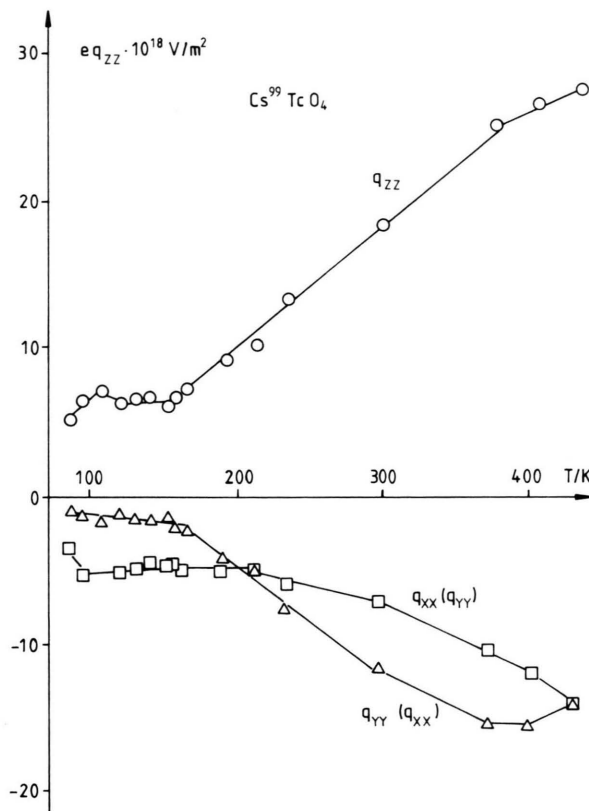

Fig. 3. The EFG tensor components at the technetium site in CsTcO$_4$ vs. temperature.

components, $|q_{ij}(T)|$, diminish with diminishing temperature. Up to date there is no comprehensive theory describing the anomalous temperature dependence of $|q_{ij}|$. Several possible mechanisms are usually considered (e.g. [8] and ref. therein). For CsTcO$_4$, the most relevant mechanisms are:

(i) orientational change of the principal axes system of the ^{99}Tc EFG tensors, since $\partial\eta/\partial T \neq 0$; and

(ii) a large negative pressure coefficient $(\partial v_Q/\partial P)_T$ in the Kushida-Benedek-Bloembergen theory [9].

^{133}Cs NMR

The observed complicated ^{133}Cs NMR line shape for CsTcO$_4$ was considered to be a superposition of two partially overlapping multiplets from the first-order quadrupole coupling (Figure 4). Hence, there are two nonequivalent cesium positions in the lattice, Cs (1) and Cs (2). Figure 4 shows also, as an example, the specific points v_{sg} and v_{st} for these two magneti-
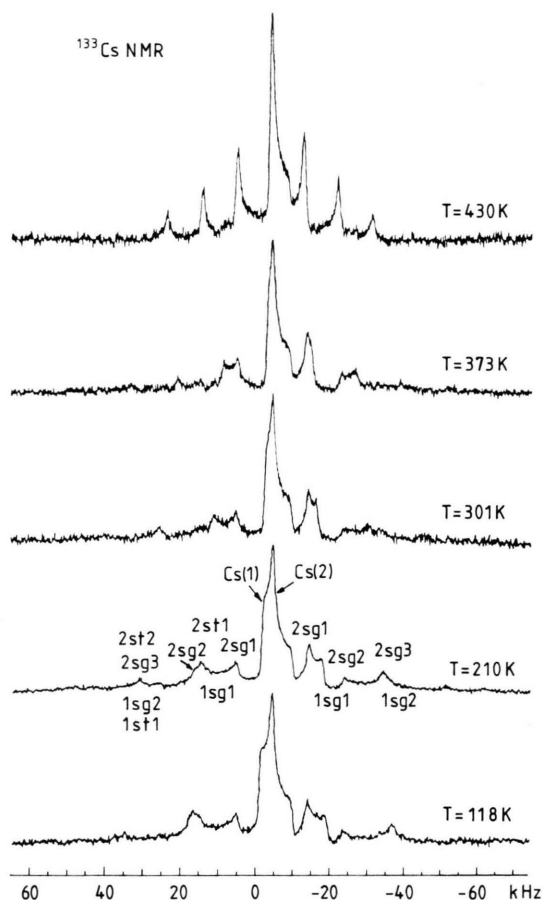
Fig. 4. ^{133}Cs NMR spectra (39.8 MHz) of polycrystalline CsTcO$_4$ at different temperatures; sweep range: spectral width = 500 kHz; number of scans = 100.

Fig. 5. Temperature dependences of the ^{133}Cs QCC (○, ●) and ^{133}Cs chemical shifts (△, ▲) for different cesium positions.

cally nonequivalent cesium positions at 210 K. The line shape analysis was carried out assuming a negligible value of η (< 0.05).

The estimations of the line intensity ratio, which where carried out by comparing the central components or satellites, have given evidence of a decrease of the Cs(1) site population with increasing temperature, while the population of the Cs(2) sites increases. At 430 K only the Cs(2) position is occupied. At 118 K the isotrope ^{133}Cs chemical shifts for the Cs(1) and Cs(2) positions are (-50 ± 20) ppm and (-120 ± 20) ppm, respectively, the Cs(2) site being characterized by a magnetic shielding anisotropy. Temperature increase caused practically no changes in the anisotropy parameters and the ^{133}Cs chemical shift for the Cs(2) position, while the signal of Cs(1) monotonously shifted to the high field side, so that at 430 K the
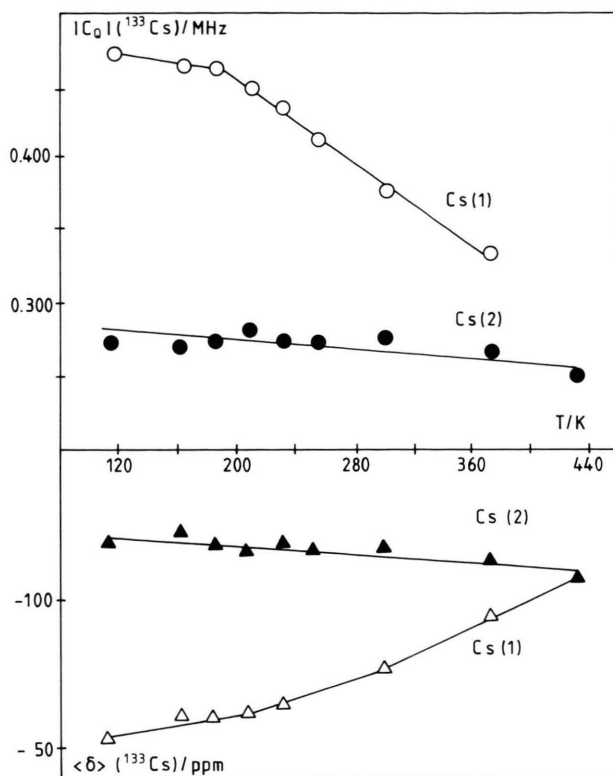
chemical shifts of both, Cs(1) and Cs(2), coincided (Figure 5). The magnetic shielding anisotropy at 430 K has the following parameters: $\sigma_1 = -85$; $\sigma_2 = -105$; $\sigma_3 = -230$, $\langle \delta \rangle^{iso} = (-140 \pm 10)$ ppm.

Figure 5 shows the temperature dependence of the ^{133}Cs QCC's for the two positions of cesium nuclei. The ^{133}Cs QCC values differ from each other in magnitude as well as in temperature behaviour. The ^{133}Cs QCC of the Cs(1) nuclei linearly diminishes from 118 to 190 K with a coefficient

$$\frac{1}{v_Q^0} \cdot \frac{\Delta v_Q}{\Delta T} = -0.5 \cdot 10^{-4} \text{ K}^{-1},$$

where v_Q^0 [Cs(1)] = 35.2 kHz and C_Q^0 [Cs(1)] = 0.49 MHz.

In the interval 190–200 K a break of $C_Q(T)$ takes place (Figure 5). In the temperature range 200–380 K a linear descent of $v_Q(T)$ with a coefficient $\Delta v_Q/\Delta T = -0.07$ kHz K^{-1} was observed.

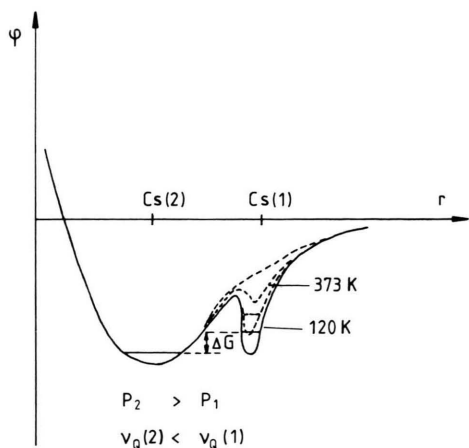The Cs(2) position is characterized by a linear decrease of $v_Q(^{133}$Cs) over the whole temperature inter-

Fig. 6. Schematic drawing showing the temperature behaviour of the crystal potential, φ, at the cesium positions.

val (100–430 K) with a coefficient

$$\frac{1}{v_Q^0} \cdot \frac{\Delta v_Q}{\Delta T} = -3.4 \cdot 10^{-4} \, \text{K}^{-1},$$

where $v_Q^0 [\text{Cs}(2)] = 20.85$ kHz and $C_Q^0 = 0.29$ MHz.

The results of ^{133}Cs NMR study lead to the following conclusions:

(i) two crystallographically and magnetically non-equivalent cesium positions are present in the structure. The magnetic nonequivalence is manifested by different values of the ^{133}Cs chemical shifts for Cs(1) and Cs(2), and the structural one by the different

^{133}Cs QCC values in Cs(1) and Cs(2) positions. The presence of two positions in the CsTcO$_4$ lattice is a result of a disordering of cesium ions within Pnma space group.

(ii) The population ratio of the Cs(1) and Cs(2) positions is dominated by the difference between the free energies of these states:

$$\frac{p_2}{p_1} = \exp\left(\frac{\Delta G}{RT}\right).$$

A crude estimations of line intensities ($\pm 40\%$) has given the following values of p_2/p_1 and ΔG:

T, K	118	210	301	373
p_2/p_1	2	4	5	6.5
ΔG, kJ mol^{-1}	0.68	2.4	4.0	5.8

(iii) The origin of the cationic position splitting seems to be a double minimum potential, φ, of a crystal field in the vicinity of cesium sites. Some difference between the minimum depths follows from the estimations of ΔG values given above; a different potential steepness for the Cs(1) and Cs(2) positions is determined by the expressions

$$v_Q \sim \partial^2 \varphi / \partial r^2, \quad \text{when} \quad v_Q[\text{Cs}(2)] > v_Q[\text{CS}(1)].$$

With temperature growth a gradual transition from the double minimum potential to a single minimum potential takes place (Figure 6). This process is accompanied by a structural phase transition from orthorhombic with splitted cationic positions to tetragonal.

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