[heat capacity from CF] supplementary to {13.1:434}

Once the crystal-field (CF) structure is determined, for example by neutron scattering, the CF contribution to the heat capacity can be calculated according to

$$C_{CF} = \frac{1}{Zk_BT^2}\left[\sum_n d_n E_n^2 \exp\left(-E_n/k_BT\right) - \frac{1}{Z}\left(\sum_n d_n E_n \exp\left(-E_n/k_BT\right)\right)^2\right], \quad (1)$$

where

$$Z = \sum_n d_n \exp\left(-E_n/k_BT\right) \quad (2)$$

is the partition function, and E_n is the energy of the n^{th} CF level.

The calculated C_{CF} is shown in Figure 1 below. The Schottky-like peaks in the specific heat at approximately 20 and 100 K are the results of low-lying crystal-field states in $TmPO_4$.

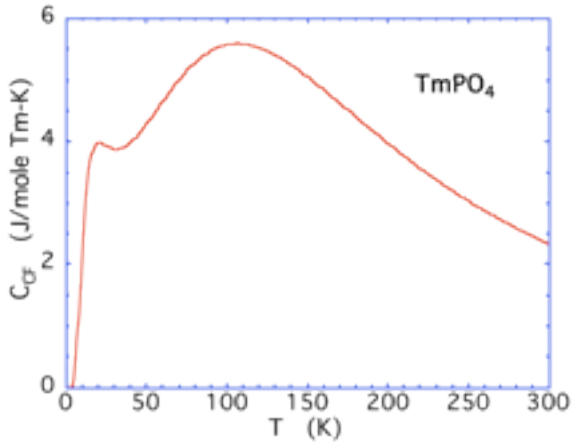

Figure 1. The calculated contribution to the specific heat of $TmPO_4$ from the Tm^{3+} crystal-field states.

In real systems, the RE ions are not isolated from each other or completely inert to the environment. The crystal-field states partake electron-lattice interactions, magnetic-moment fluctuations, or cooperative phase transformations. Within the RPO_4 and RVO_4 series of the zircon structure, several members exhibit f-electron-lattice coupling, magnetostriction, anomalous elasticity, and cooperative Jahn-Teller phase transition. Neutron spectroscopy remains to be one of the most powerful methods for investigations of these phenomena.

Reference:

Loong, C-K., L. Solderholm, M. M. Abraham, L. A. Boater, and N. M. Edelstein (1993), "Crystal-field excitations and magnetic properties of $TmPO_4$", *J. Chem. Phys.* **98**, 4214.