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Interplay between Tm^{3+} and Cr^{5+} magnetic sublattices in $TmCrO_4$

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Abstract

The compound $TmCrO_4$ has been studied with bulk magnetization measurements, ^{169}Tm Mössbauer spectroscopy and muon spin relaxation (μSR). The Cr sublattice in $TmCrO_4$, which orders with a second-order magnetic phase transition at $T_C = 18.75$ K, gradually induces magnetic order in the non-magnetic crystal field ground state of the Tm sublattice.

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Rare earth chromates belong to the group of tetragonal compounds (space group $I4_1/amd$) with the general formula RXO_4, where X = V, P, As and Cr. The $RCrO_4$ oxides allow us to study the magnetic interaction between the Cr^{5+} ($S = \frac{1}{2}$) and R^{3+} sublattices. In this paper, we will restrict ourselves to $TmCrO_4$. Magnetic susceptibility measurements have determined the magnetic ordering temperature to be about 19 K [1]. Neutron diffraction measurements performed at $T = 2$ K, well below the magnetic ordering temperature, reveal a canted magnetic structure, where the Cr and Tm sub-lattice magnetizations have a dominant ferromagnetic contribution parallel to the *c*-axis superposed to an antiferromagnetic component in the *a–b* plane. The Cr and Tm magnetic moments have magnitudes of 1.14 and 3.13 μ_B and are oriented at angles of 34° and 5° from the *c*-axis, respectively [1]. The Tm magnetic moment is very small compared to the free ion value of 7 μ_B. Therefore, it is of interest to study $TmCrO_4$ further.

The ^{169}Tm Mössbauer spectra for $TmCrO_4$ are shown in Fig. 1. At $T = 28$ K, two quadrupole-split doublets were observed with an intensity ratio of about 80% to 20%. The values of the quadrupole splittings, $\Delta E_Q = |\frac{1}{2} eQV_{zz}|$ (where $Q = -1.2$ b, the quadrupole moment of the ^{169}Tm nucleus and V_{zz} the electric field gradient) are 42(6) and 112(6) mm/s, respectively. This result implies that there are two non-equivalent crystallographic sites. Due to broadening caused by the magnetic induction of the Cr^{5+} sublattice at $T = 17$ and 18 K, only one quadrupole splitting could be resolved, with a fitted quadrupole splitting of 86(3) mm/s. With decreasing temperature, two magnetically split sextets appear in coexistence with the two paramagnetic doublets. Again, they have a relative intensity ratio of about 80% to 20%, and both their magnetic splitting and their intensity relative to the paramagnetic doublets grow as the temperature decreases. Coupled with the hysteresis observed for the magnetization curves [2], this behaviour is the characteristic of a first-order magnetic transition

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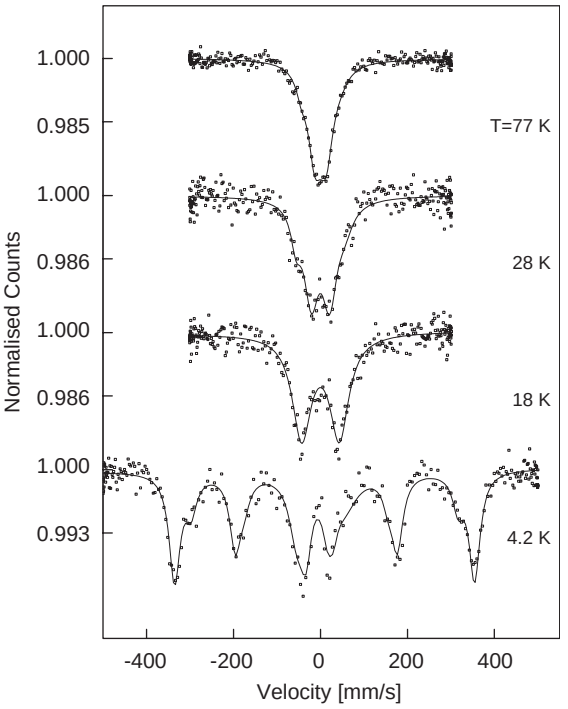

Fig. 1. Temperature dependence of the ^{169}Tm Mössbauer spectra measured from 4.2 up to 77 K. The spectra are analyzed with two sites. The spectrum at $T = 4.2$ K consists of two magnetic sextets and a non-magnetic doublet.

for the Tm sub-lattice of $TmCrO_4$. At $T = 4.2$ K, the residual paramagnetic doublets comprise about 25% of the total spectrum intensity, but are not well resolved. However, the outer lines of the two sextets are clearly resolved with a magnetic splitting of 412(1) T for the more intense sextet and 367(1) T for the less intense sextet. Given that the magnetic hyperfine field for the Tm^{3+} free ion value is 662.5 T [3], the corresponding magnetic moments are 4.4 and 3.9 μ_B, respectively. Since the axes of the direction of the hyperfine field and the principal electric field gradient are almost coaxial as shown above, the fitted quadrupole interactions correspond to $\frac{1}{2}eQV_{zz} \approx 18.6(6)$ mm/s for both sextets. Based on the ^{155}Gd Mössbauer spectroscopy results reported elsewhere for isostructural $GdCrO_4$ [2] and point charge calculations we found a negative value for the rank 2 crystal field Stevens parameter corresponding to a positive lattice contribution to the electric quadrupole interaction. Then, the 4f contributions to the ^{169}Tm quadrupole interaction are estimated to be $\frac{1}{2}eQV_{zz}(4f) \approx +12.0$ and -7.1 mm/s for the sextets with intensity ratio 80% and 20%, respectively. By comparison, the free ion 4f value of $\frac{1}{2}eQV_{zz}(4f)$ is equal to 176 mm/s [3], suggesting that strong crystal field quenching is involved for $TmCrO_4$.

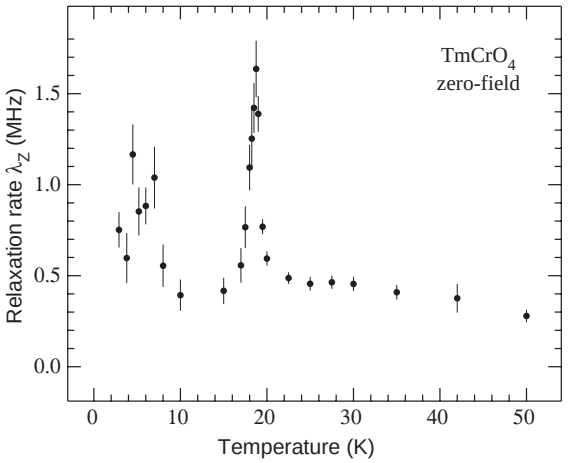

Fig. 2. Temperature dependence of the μSR relaxation rate λ_Z. At $T = 18.75$ K the λ_Z has a sharp maximum, indicating a magnetic phase transition.

The muon depolarization vs. time of the $TmCrO_4$ compound has been measured between 1.85 and 50 K. No evidence of spontaneous magnetic precession could be found in the muon spectra. The measured spectra could be well described by an exponential depolarisation function characterized by a relaxation rate λ_Z. As shown in Fig. 2 λ_Z exhibits a maximum at $T_C = 18.75$ K, concomitant with a loss of $\frac{2}{3}$ of the amplitude of the signal (not shown) measured in the paramagnetic regime. We assume that T_C corresponds to the critical temperature of the Cr sublattice. Besides, a second broader anomaly is present below 8 K probably due to the gradual Tm magnetic ordering as mentioned above.

From the μSR and ^{169}Tm Mössbauer measurements shown above one can conclude that the Cr sublattice orders with a second-order magnetic phase transition at $T_C = 18.75$ K. Since the Tm sublattice orders gradually at lower temperatures with a first-order magnetic phase transition, one can expect that the crystal field scheme has a non-magnetic singlet ground state with e.g. an eigenfunction $a|-4\rangle + b|0\rangle - c|+4\rangle$ with $c = a$. Under influence of magnetic exchange this eigenfunction will purify in the direction of $|-4\rangle$, which corresponds with a magnetic moment of 4.67 μ_B. The magnetic moments found above are slightly smaller than this value. The theoretical 4f contribution to the quadrupole interaction is calculated to be $\frac{1}{2}eQV_{zz} \approx +16$ mm/s for a pure $|-4\rangle$ ground state. As expected, this value is higher than the values mentioned above.

In contrast with $TmVO_4$ [4] and $TmAsO_4$ [5], which show Jahn–Teller transitions due to doublets as ground states, $TmPO_4$ [4] does not show this effect due to a singlet ground state. On the other hand, the occurrence of two slightly different crystallographic Tm sites even at $T = 28$ K may be indicative of a Jahn–Teller transition in $TmCrO_4$.

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