NMR investigation of spin flip in $TmCrO_3$

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The double-pulse NMR technique is used to study spin flip in the rare-earth orthochromite $TmCrO_3$. It is shown that in the absence of an external magnetic field, spin flip for $T < 5.6$ K takes place as a first-order phase transition from a high-temperature (Γ_2) to a low-temperature phase (Γ_4), the two phases coexisting in a temperature interval larger than 3.8 K. The spin flip phase transitions $\Gamma_2 \leftrightarrow \Gamma_4$ induced by an external magnetic field and the accompanying effects due to the magnetic and electric inequivalence of the ^{53}Cr nuclei in different magnetic sublattices are investigated. The experimental data are used to calculate the anisotropy parameters for the hyperfine and nuclear quadrupole interactions.

INTRODUCTION

Much work has been done on the magnetic structure and magnetic properties of thulium orthochromite ($TmCrO_3$).[1–6] Below the Néel temperature $T_N = 124$ K, this material has a weakly ferromagnetic moment along the a axis with the $\Gamma_2(F_x, C_y, G_z)$ magnetic configuration. A cancellation of the magnetic moments due to the antiparallel alignment of the f- and d-sublattice magnetizations is found to occur at $T_k \approx 29$ K (Refs. 2,3). The low-temperature magnetic properties of $TmCrO_3$ are particularly difficult to interpret. Thus, according to the data in Ref. 2, the Γ_2 configuration should persist down to $T \sim 2$ K; however, the critical fields for the transition to the $\Gamma_4(G_x, A_y, F_z)$ configuration for $T = 2$–6 K are very small (~ 500 Oe), which makes it difficult to identify the magnetic structure unambiguously by means of ordinary magnetic measurements. The susceptibility χ_c was found to have a sharp peak at $T = 5$ K in Ref. 3, where it was attributed to ordering of the Tm^{3+} sublattice. A spin-flip transition of the type $\Gamma_2 \leftrightarrow \Gamma_4$ was also observed there at lower temperatures $T < T_2$, for T_2 between 2 and 4.2 K. The neutron diffraction results for $TmCrO_3$ also give contradictory results. According to the data in Ref. 1, the Γ_4 magnetic configuration occurs at $T = 4.2$ K, whereas more recent work[5] suggests that the Γ_2 configuration is more likely, although the experimental results are not completely self-consistent. Results from a Mössbauer (^{169}Tm) analysis of $TmCrO_3$ were reported in Ref. 6. No unusual behavior associated with ordering of the Tm sublattice was detected in the γ-resonance spectrum down to $T = 1.4$ K. Hodges *et al.*[6] regarded their results as supporting the conclusion reached in Ref. 1 on the existence of a spin-flip transition at $T \gtrsim 4.2$ K from a low-temperature configuration Γ_4 to a high-temperature angular phase Γ_{42} (G_{xz}). The low-temperature properties of $TmCrO_3$ thus remain unclear.

We believe that NMR measurements using the ^{53}Cr nuclear isotope can play a decisive role in clarifying the situation here. This technique has proven to be among the most precise and effective methods for studying the properties of spin-flip transitions in orthoferrites and orthochromites.[7,8] In addition, NMR can provide a wealth of information regarding the anisotropy of the hyperfine interactions, which is particularly pronounced near spin-flip transitions when the nuclei from different sublattices are inequivalent magnetically and electrically.[7,8]

In this paper we discuss the ^{53}Cr NMR spectra for $TmCrO_3$ at temperatures down to 1.8 K both with and without an external magnetic field applied parallel to the a or c crystallographic axes. The experimental results allow us to uniquely identify the low-temperature magnetic structure of $TmCrO_3$ and also provide much information on the anisotropy parameters for the magnetic hyperfine interactions and on the components of the electric field gradient tensor for the ^{53}Cr nuclei.

1. ^{53}Cr NMR SPECTRUM IN $TmCrO_3$ IN THE ABSENCE OF AN EXTERNAL MAGNETIC FIELD

We investigated $TmCrO_3$ single crystals containing natural amounts of the ^{53}Cr isotope; the crystals were grown by spontaneous crystallization from a solution in a melt. The spin echo signals corresponded to excitation of the nuclear spins inside the domains; the optimum excitation pulse lengths were $\tau_1 = 5\,\mu$s and $\tau_2 = 10\,\mu$s, with a repetition rate of 10 Hz.

Analysis of the ^{53}Cr NMR spectra reveals that the low-temperature behavior of $TmCrO_3$ is quite unusual (Fig. 1). Three lines are observed at temperatures above $T = 5.6 \pm 0.1$ K; the conditions under which they are excit-

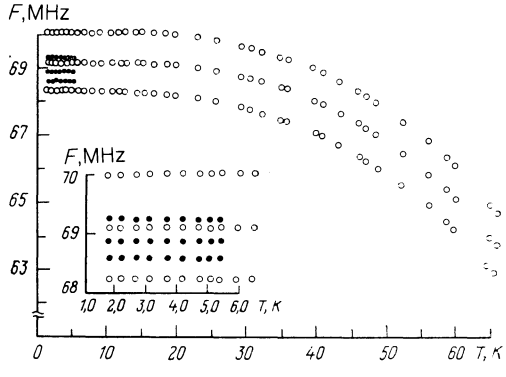

FIG. 1. Temperature dependence of the NMR frequencies for ^{53}Cr nuclei in $TmCrO_3$; the insert shows $F(T)$ near the spin-flip transition temperature for $TmCrO_3$: ○, high-temperature phase; ●, low-temperature phase.

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ed (H_{pr} parallel to the c axis) indicate that they are associated with a Γ_2 high-temperature phase, in complete agreement with the magnetic and neutron-diffraction results in Refs. 2–5. The quadrupole splitting ~ 0.88 MHz is close to the value 1.1 MHz found for the Γ_2 configuration in $GdCrO_3$ (Ref. 7).

When T drops below 5.6 K, these lines are supplemented by three new NMR lines with a quadrupole splitting ~ 0.34 MHz. The intensity of the new lines increases as T decreases and at $T = 1.8$ K becomes comparable to the intensity of the lines observed for $T > 5.6$ K. Such behavior corresponds to a first-order phase transition.

The magnitude of the quadrupole splitting in the low-temperature phase in $TmCrO_3$ is similar to the quadrupole splittings for the Γ_4 configuration in the orthochromites $ErCrO_3$ (0.45 MHz), $GdCrO_3$ (0.47 MHz), and $YCrO_3$ (0.5 MHz) Refs. 7,9). Together with the fact that the NMR was excited with H_{pr} parallel to the a axis, this indicates that the low-temperature phase had the Γ_4 configuration, in agreement with the magnetic and neutron-diffraction data in Refs. 1–4, which also suggest a Γ_4 low-temperature configuration for $TmCrO_3$.

Since only three new additional lines appeared in the spectrum and the positions of the three high-temperature lines remained unchanged below $T = 5.6$ K, the formation of a Γ_{24} angular phase can be ruled out (this also follows from the temperature dependence of the line intensities). We note that the NMR spectrum was well-resolved for both the high- and the low-temperature phases (the linewidths were ~ 100 kHz and ~ 120 kHz, respectively).

The low-temperature properties of $TmCrO_3$ thus correspond to a first-order spin-flip transition of the type $\Gamma_2 \leftrightarrow \Gamma_4$ in which the two phases coexist for T between $T_> = 5.6$ K and $T_< < 1.8$ K. It is natural to attribute the unusual breadth of the transition and the "freezing" of the high-temperature phase to saturation of the Tm-sublattice for $T \lesssim 4.2$ K (Ref. 6) and to the weak temperature dependence of the effective magnetic anisotropy constants.

Measurements of the temperature dependence of the ^{53}Cr NMR frequencies did not reveal any hysteresis when the specimen was heated or cooled. Since hysteresis is generally typical for first-order phase transitions, this indicates that the rearrangement of the domain structure was reversible near the transition temperature and involved nucleation of the new phase in 180-degree domain walls consisting of the "old" phase.[10]

2. ^{53}Cr NMR SPECTRA IN $TmCrO_3$ IN AN EXTERNAL MAGNETIC FIELD

Additional support for the above identification of the low-temperature magnetic structure in $TmCrO_3$, as well as information on the anisotropy of the magnetic and electric hyperfine transitions for ^{53}Cr nuclei, can be obtained by analyzing how the ^{53}Cr NMR spectrum in $TmCrO_3$ is affected by an external magnetic field.

For example, the theory in Ref. 10 predicts that an external magnetic field H parallel to the c axis should alter the first-order $\Gamma_2 \leftrightarrow \Gamma_4$ spin-flip transition that occurs in zero magnetic field. Initially, as the temperature drops to $T = 5.6$ K but remains above a critical temperature T_B, the transition should occur smoothly, with a continuous expansion of all of the Γ_{24} angular configurations. The nature of the transition should change for $T < T_B$—there should be a range of temperatures for which the angular (Γ_{24}) and the final (Γ_4) phases coexist.

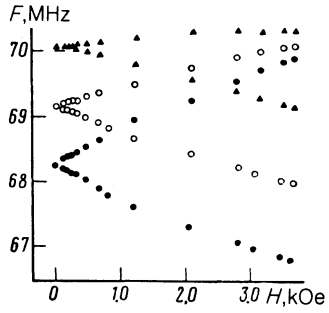

FIG. 2. NMR frequency for ^{53}Cr nuclei in the high-temperature phase ($T = 10.8$ K, magnetic field H parallel to the c axis).

Our measurements for $TmCrO_3$ showed that the $\Gamma_2 \leftrightarrow \Gamma_4$ spin-flip transition in an external magnetic field $H \| c$ does in fact behave in this way. Figure 2 shows the experimental dependence of the ^{53}Cr NMR frequencies for $TmCrO_3$ at $T = 10.8$ K as a function of the external magnetic field H (H was parallel to the c axis and H_{pr} was parallel to the a axis). The dependence $F(H)$ is quite characteristic and indicates that the Cr^{3+} spins rotated continuously in the a,c plane up to fields $H = 3.5$ kOe (the NMR line intensities dropped abruptly at higher fields).

When the temperature decreased to nearly $T_> = 5.6$ K ($T = 6.9$ K in Fig. 3), the dependence $F(H)$ for weak external fields H parallel to the c axis remained essentially unchanged. New NMR lines appear in the spectrum when $H \gtrsim 1$ kOe which can be unambiguously assigned to the Γ_4 low-temperature phase (H_{pr} was parallel to the a axis, and the quadrupole splitting was ~ 0.34 MHz); their intensity increases with H. The angular Γ_{24} phase thus coexists with the Γ_4 phase in $TmCrO_3$ for $T = 6.9$ K and $H \gtrsim 1$ kOe, as predicted theoretically in Ref. 10.

Similar behavior was observed at $T = 5.6$ K and in the low-temperature region, as can be seen from Fig. 4, which plots $F(H)$ for the high-temperature phase at $T = 3.5$ K (H and H_{pr} both parallel to the c axis).

We also investigated $F(H)$ for the low-temperature phase (H_{pr} along the a axis) when the external field H was parallel to the a axis (Fig. 5). Unlike the situation for the high-temperature phase, the low-frequency spectral line was not split, and the weak high-frequency line disappeared almost immediately at low fields.

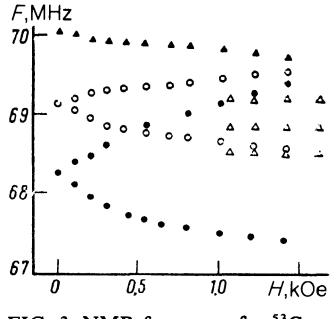

FIG. 3. NMR frequency for ^{53}Cr nuclei near the spin-flip transition in $TmCrO_3$ induced by an external magnetic field ($T = 6.9$ K, H parallel to the c axis); ▲, ●, ○ give values for the high-temperature phase, △ corresponds to the low-temperature phase.

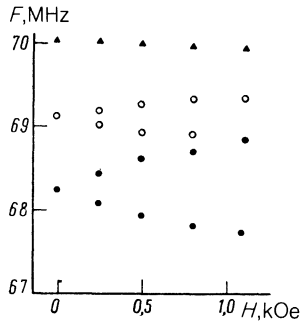

FIG. 4. Field dependence of the NMR frequencies for ^{53}Cr nuclei in the high-temperature phase ($T = 3.5$ K, $H \| c$).

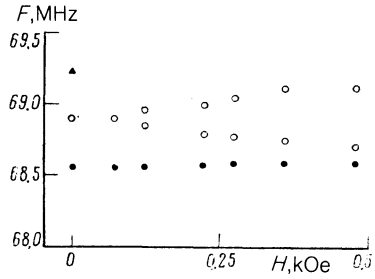

FIG. 5. Field behavior for $T = 1.9$ K, H parallel to the a axis.

In addition to confirming our interpretation of the low-temperature magnetic structure and spin-flip transition, the analysis of the field dependence of the ^{53}Cr NMR frequencies in the high- and low-temperature phases in $TmCrO_3$ also yields quantitative information about the anisotropy parameters for the magnetic hyperfine interactions and about the components of the electric field gradient tensor for the ^{53}Cr nuclei. For example, the theory developed in Refs. 7 and 8 gives

$$\begin{aligned}
&\delta E(^1/_2 \rightarrow -^1/_2) = 2[a_{xz} \sin 2\theta + \gamma_n H \cos\theta] \quad \text{(center line)} \\
&\delta E(^3/_2 \rightarrow ^1/_2) = 2[(a_{xz} - v_{xz}) \sin 2\theta + \gamma_n H \cos\theta] \\
&\qquad\qquad \text{(side lines)} \\
&\delta E(-^1/_2 \rightarrow -^3/_2) = 2[(a_{xz} + v_{xz}) \sin 2\theta + \gamma_n H \cos\theta],
\end{aligned} \tag{1}$$

for the splittings of the three ^{53}Cr NMR lines in an orthochromite in an external H field parallel to the c axis. Here γ_n is the nuclear gyromagnetic ratio, θ is the angle between the c axis and the Cr^{3+} spins, a_{xz} is the anisotropy parameter for the magnetic hyperfine interactions,[7] and

$$v_{xz} = 3eQV_{xz}/2I(2I-1) = {}^1/_2 eQV_{xz},$$

where Q is the nuclear quadrupole moment and V_{xz} is the xz-component of the electric field gradient tensor.

The shifts in the resonance lines are given by[7]

$$\begin{aligned}
&\Delta f(^1/_2 \rightarrow -^1/_2) = -(a_{xx} \sin^2\theta + a_{zz} \cos^2\theta) \quad \text{(center line)} \\
&\Delta f(^3/_2 \rightarrow ^1/_2) = [\Delta f(^1/_2 \rightarrow -^1/_2) - (v_{xx} \sin^2\theta + v_{zz} \cos^2\theta)] \\
&\qquad\qquad \text{(side lines)} \\
&\Delta f(-^1/_2 \rightarrow -^3/_2) = [\Delta f(^1/_2 \rightarrow -^1/_2) + (v_{xx} \sin^2\theta + v_{zz} \cos^2\theta)],
\end{aligned} \tag{2}$$

The parameters v_{xx} and v_{zz} determine the quadrupole splitting in the Γ_4 and Γ_2 phases, respectively. Table I lists values for v_{xx}, v_{yy}, and v_{zz} ($v_{xx} + v_{yy} + v_{zz} = 0$) calculated in the point-lattice model[7] for Nd, Tb, Dy, and Er orthochromites with known crystallographic parameters, as well as experimental values of v_{ii} for Gd, Er orthochromites (Refs. 7,9) and our values for $TmCrO_3$; the behavior of the signs is as expected for members of the orthochromite series.

According to Eq. (1), the parameters a_{xz} and v_{xz} determine the size of the NMR splitting and its angular dependence. The theoretical relations (1) and (2) accurately approximate the experimental data in Figs. 2 and 3 if we take

$$\begin{aligned}
|a_{xz}| &= 0.34 \text{ MHz} \quad |v_{xz}| = 0.46 \text{ MHz} \quad (T = 10.8\text{K}), \\
|a_{xz}| &= 0.22 \text{MHz} \quad |v_{xz}| = 0.46 \text{ MHz} \quad (T = 6.9\text{ K}).
\end{aligned}$$

The component v_{xz} of the electric field gradient tensor is thus found to be nearly independent of T, while the anisotropy parameter a_{xz} of the hyperfine interaction decreases appreciably with temperature. This is not surprising if we recall that the field gradient tensor for the ^{53}Cr nucleus is essentially independent of the magnetic state of the rare-earth ions, whereas the data in Ref. 8 indicate that the Tm^{3+} ions may give an appreciable temperature-dependent contribution to the anisotropy of the magnetic hyperfine interactions.

The high-frequency NMR line is not split at $T = 6.9$ K in an external field H parallel to the c axis (Fig. 3). This is a straightforward consequence of the random cancellation of the contributions to δE from the external magnetic field and from the magnetic and electric inequivalence of the nuclei.

The shifts of the center line in the NMR spectra for the high- and low-temperature phases in $TmCrO_3$ lead to the value

$$|a_{xx} - a_{zz}| = 0.21 \text{ MHz}$$

which also characterizes the anistropy of the magnetic hyperfine interactions. We note that $|a_{xx} - a_{zz}| = 0.5$ MHz for $GdCrO_3$ (Ref. 7).

CONCLUSIONS

Our studies of the temperature and field behavior of the ^{53}Cr NMR spectrum in the orthochromite $TmCrO_3$ enabled

TABLE I. Components of the electric field gradient tensor near ^{53}Cr nuclei in $RCrO_3$.

$RCrO_3$	v_{zz}	v_{xx}	v_{yy}	$RCrO_3$	v_{zz}	v_{xx}	v_{yy}
$NdCrO_3$	1,35	−0,32	−1.03	$ErCrO_3$	−0,58	−0,17	0,75
$GdCrO_3$ *	1,10	−0,47	−0,63	$ErCrO_3$ *	−0,45	−0,19	0,64
$TbCrO_3$	0.37	−0,40	0,03	$TmCrO_3$ *	−0,88	−0,34	1,22
$DyCrO_3$	0,00	−0,15	0,15				

*Experimental values.

us to demonstrate that a first-order spontaneous spin-flip transition occurs from a high-temperature Γ_2 magnetic configuration to a low-temperature Γ_4 magnetic configuration, and that both phases are present for T between $T_> = 5.6$ K and $T_< < 1.8$ K. The theory predicts that an external magnetic field H parallel to the c axis should induce a $\Gamma_2 \leftrightarrow \Gamma_4$ spin-flip transition which for $T > 5.6$ K should involve a continuous rotation of the spins; the angular (Γ_{24}) phase and the final (Γ_4) phase may coexist for certain temperatures and fields. We found that the magnetic and electric inequivalence of the ^{53}Cr nuclei from different magnetic sublattices splits the NMR lines for temperatures and fields corresponding to the Γ_{24} configuration (in which the Cr^{3+} spins rotate continuously). Finally, the components of the electric field gradient tensor and the anisotropy parameters for the magnetic hyperfine interactions were found quantitatively by analyzing the NMR spectra in the Γ_2, Γ_4 configurations and their field behavior.

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