Observation of bottleneck effect in NMR in rare-earth orthochromites

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We measured the nuclear magnetic relaxation times in the orthochromites $EuCrO_3$ and $YCrO_3$ at helium temperatures. A large (by up to 10^2) difference was observed between the spin-lattice relaxation times determined by measuring the repetition frequency of a train of excited pulses and by using the stimulated-echo method. It is shown that this difference can be attributed to the bottleneck effect.

We report here an investigation of the magnetic relaxation of ^{53}Cr spins in the orthochromites $EuCrO_3$ and $YCrO_3$. Our results are unusual in that the spin-echo signals (at temperatures ≈ 2 K) could be observed only at very low repetition frequencies of the exciting-pulse trains. The nuclear spin-lattice relaxation times T_1 determined from these frequencies were found to be much longer than the values of T_1 obtained by using stimulated echo. For $EuCrO_3$, for example, this difference reaches two orders of magnitude. We attribute this anomaly of T_1 to the onset of bottleneck effects.

SAMPLES AND EXPERIMENT

Rare-earth orthochromite crystals have a D_{2h}^{16} crystal symmetry, with the ground states of Eu^{3+} and Y^{3+} nonmagnetic in these compounds. The single crystals investigated were grown by spontaneous crystallization from the molten solution, with natural content of the ^{53}Cr isotope. In contrast to the previously investigated[1] erbium orthochromite $EuCrO_3$, the orthochromites investigated here had no orientational phase transitions.

The time T_2 of the transverse nuclear magnetic relaxation was measured by the traditional two-pulse technique (Hahn's method). The time T_1 of the longitudinal nuclear magnetic relaxation was measured both by the three-pulse "stimulated echo" method and by determining the repetition frequency of the exciting pulse pairs. Owing to the low repetition frequencies of the pulse pairs and triplets, a memory oscilloscope was used to record the NMR signals.

The optimal durations of the exciting pulses for $EuCrO_3$ were $\tau_1 = 15\ \mu s$ and $\tau_2 = 30\ \mu s$ for two-pulse echo and $\tau_1 = \tau_2 = \tau_3 = 15\ \mu s$ for three-pulse stimulated echo.

The times for $YCrO_3$ were different, viz., $\tau_1 = 10$ and $\tau_2 = 20\ \mu s$ for two-pulse echo and $\tau_1 = \tau_2 = \tau_3 = 15\ \mu s$ for three-pulse echo. Under these conditions, the two-pulse echo signals have spectra consisting of fully resolved quadrupole multiplets (the spin of ^{53}Cr is $I = 3/2$).

The quadrupole splitting between the central line and each of the sideband lines was ≈ 340 and ≈ 500 for $EuCrO_3$ and $YCrO_3$, respectively. The corresponding linewidths at half maximum were ≈ 30 and ≈ 60 kHz. The NMR linewidths did not change noticeably in the temperature range investigated. It can be deduced from the behavior of the spectra in the magnetic field that the echo signals are due to nuclei located in domains rather than in domain walls. The measurements were made in the temperature intervals 1.8–4.2 K for $EuCrO_3$ and 1.8–12 K for $YCrO_3$. The temperature was monitored by a semiconductor sensor attached directly to the sample, so that effects connected with sample heating were completely excluded.

RESULTS

The two-pulse echo signals from $EuCrO_3$ were observed at a pulse-pair repetition frequency 16 Hz, with the pulse carrier frequencies varying smoothly. When the carrier frequency became comparable with the NMR frequency, an echo-signal burst was observed on the oscilloscope screen, but its lifetime was too short to be immediately noticeable. This means that the first two or three pairs of resonant pulses saturate completely the nuclear spin system, whereas the pulses with close frequencies do not influence the state of the sample. Using a memory oscilloscope, we succeed in observing the signal of one pulse pair. The signal intensity was fully restored if the next pair was applied after 60 s (i.e., at a repetition frequency 0.02 Hz). This enabled us to measure the characteristic settling time of the nuclear-spin thermal equilibrium from the dependence of the echo-signal intensity on the pulse-pair repetition frequency.[2–4]

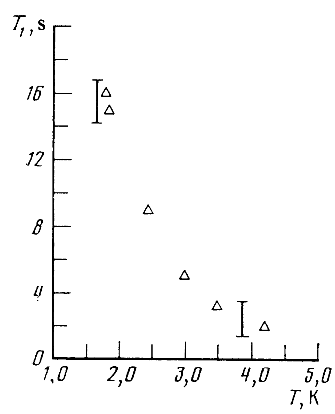

FIG. 1. Temperature dependence of the longitudinal relaxation time in $EuCrO_3$, determined by measuring the pulse-pair repetition frequency.

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The results of such measurements for $EuCrO_3$ are shown in Fig. 1. It can be seen that this time increases rapidly with decreasing temperature. The time T_1 measured for the sample by the three-pulse stimulated-echo technique was found to be 0.2 s at $T = 1.8$ K. It could not be measured at higher temperatures in view of the weakness of the stimulated-echo signal. The times T_1 obtained by the two procedures thus differ by two orders of magnitude.

The difference is similar also for $YCrO_3$, but is much less pronounced. The plots of T_1 vs temperature in Figs. 1 and 2 are given only for the central component of the multiplet, but are similar for the sidebands. Figure 3 shows the measured times T_2 of the transverse nuclear magnetic relaxation for $EuCrO_3$ and $YCrO_3$. No particular anomalies were observed in the behavior of T_2 for these compounds.

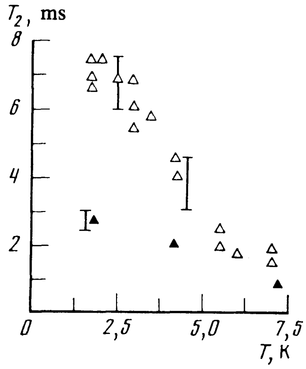

FIG. 3. Temperature dependence of the transverse relaxation time: △—$EuCrO_3$; ▲—$YCrO_3$.

DISCUSSION

Let us examine the possible causes of the indicated disparities in the values of T_1 determined from measurements of the pulse-pair repetition frequency and by the stimulated-echo technique.

1. Determination of T_1 by measuring the repetition frequency of a pulse pair[4]

This method of measuring T_1 is based on the fact that the two-pulse echo intensity is determined by the longitudinal projection of the nuclear magnetization m_z prior to the first pulse.[2] When the echo signals are excited, the vector **m** is deflected away from the **z** axis and m_z is decreased thereby. For example, after trains of $\pi/2$ and π pulses, which produce the maximum two-pulse echo signal,[2] m_z vanishes, but then returns to its equilibrium value m_0 determined by the lattice temperature, in accordance with Bloch's law[2]

$$m_z(t) = m_0[1-\exp(-t/T_1)], \tag{1}$$

so that the intensity of the echo signal from the next pair depends on the ratio of the time interval t between the pairs to the value of T_1. The value of T_1 measured by this method thus determines the time required to equalize the spin-system and lattice temperatures.

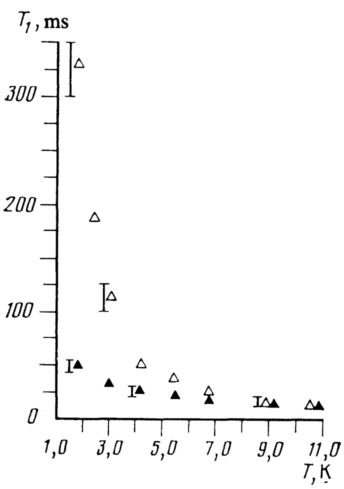

FIG. 2. Temperature dependence of the time of longitudinal relaxation in $YCrO_3$: △—determined by measuring the pulse-pair repetition frequency; ▲—results of measurements by the three-pulse technique (stimulated echo).

2. Measurement of T_1 using stimulated echo

Consider a train of three $\pi/2$ pulses, which ensures maximum stimulated-echo intensity.[2] Let the first pulse rotate the vector **m** about the **x** axis through an angle $\pi/2$. After such a $\pi/2$ pulse, the projections of the vector **m** are

$$m_x = m_z = 0, \quad m_y = m_0. \tag{2}$$

In the interval between the pulses the vector **m** precesses about the **z** axis at the NMR frequency ω_n, so that after a time τ_{12} the component of **m** at the instant when the second pulse is applied take the form

$$m_x = m_0 \sin \omega_n \tau_{12}, \quad m_y = m_0 \cos \omega_n \tau_{12}, \quad m_z = 0. \tag{3}$$

An important feature that ensures echo-signal formation in this process is that the distribution of the vectors **m** with respect to the coordinate **r** is nonuniform because of the variations of the frequency $\omega_n = \omega_n(r)$. As a result, after the second $\pi/2$ pulse the distribution is also nonuniform with respect to the projection of **m**:

$$m_z(r) = m_0 \cos \omega_n(r)\tau_{12}, \quad m_x(r) = m_0 \sin \omega_n(r)\tau_{12}, \quad m_y = 0. \tag{4}$$

It is this nonuniformity that ensures the appearance of the stimulated-echo signal after the third $\pi/2$ pulse.[2]

Owing to relaxation, however, this nonuniformity varies in the interval between the second and third pulses in accordance with Bloch's law:

$$\begin{aligned} m_z(r,t) &= m_0 + [m_z(r) - m_0] \exp(-t/T_1) \\ &= m_0\{1 + [\cos \omega_n(r)\tau_{12} - 1] \exp(-t/T_1)\}, \end{aligned} \tag{5}$$

so that the stimulated-echo intensity should depend on the ratio of the time intervals between the second and third pulse to the time T_1. Thus, the quantity measured by this method determines how long the variations are preserved in the distribution of the nuclear spins over the projections m_z.

3. Relation between the spin and lattice temperature equalization time and the time of inhomogeneity preservation in the spin system under bottleneck conditions

For the bottleneck effect[5] to exist, the equilibrium between the spin subsystem and the lattice should set in via an intermediate system. This process is characterized by two parameters: the time T_1 for thermal equilibrium to be established between the spin and the intermediate subsystems, and the time T'_1 for the temperatures of the intermediate subsystem and of the lattice to equilibrate. The bottleneck effect sets in at $T'_1 \gg T_1$.

The nonuniformity-preservation time in the spin distribution over the projections mz is determined by T_1 regardless of the ratio of T_1 and T'_1, so that the time measured by the stimulated echo method is always T_1. Thus, measurement of the pulse-pair repetition frequency yields the time T_1 in the absence of the bottleneck ($T_1 > T'_1$) and the time T'_1 under bottleneck conditions ($T_1 \ll T'_1$).

In the case of relaxation of paramagnetic impurities in crystals the role of the intermediate system is played by the so-called resonant phonons (those having a frequency $\omega_{\rm ph} \approx \omega_{\rm ESR}$). Additional research is needed to establish the nature of the intermediate subsystem in our case.

Of course, NMR data alone are not enough to deduce incontrovertibly the existence of a bootleneck. Our conclusion must thus be regarded only as a hypothesis, one that seems quite plausible to us.

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