55\textsuperscript{Mn} nuclear magnetic resonance for antiferromagnetic $\alpha$-Mn$_2$O$_3$

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**Abstract.** The zero-field 55\textsuperscript{Mn} nuclear magnetic resonance (NMR) spectra for antiferromagnetic $\alpha$-Mn$_2$O$_3$ were obtained at low temperatures. The Gaussian-shaped spectrum was positioned around 314 MHz in the zero-temperature limit, and the linewidth was about 5 MHz. The magnetic moment estimated from the resonance frequency was 2.6\textmu B per Mn$^{3+}$ ion, which corresponds to 65\% of 4\textmu B, which is expected when only the contribution of spin to the magnetic moment is considered. The temperature dependence of the sublattice magnetization does not fit Bloch’s $T^2$ law well but instead fits the exponential form applicable when there is an initial energy gap in the dispersion relation of the spin wave. From the fitting, we obtained an energy gap of 1.82 meV and an anisotropy energy of 0.22 meV. The spin–spin relaxation time measured as a function of frequency shows that the Suhl–Nakamura interaction is suppressed by this energy gap. The line broadening is mostly influenced by the dipolar hyperfine interaction.

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1. Introduction

Manganite exists in several different chemical forms, including MnO, Mn₂O₃, Mn₃O₄ and MnO₂, where the valence states of manganese ions are 2+, 3+ and 4+. All are magnetic, but their detailed magnetic properties are all different. Manganese sesquioxide (Mn₂O₃) is used in combustion catalysis, a method of reducing the emissions of organic compounds and nitrous oxide from waste gas, as an environmentally friendly and inexpensive catalyst that can replace Pt and Pd [1]. It is not only useful in practical applications but also interesting from a physical point of view. The crystal structure of α-Mn₂O₃ is a cubic bixbyite (space group Ia3) above 302 K. Below this temperature, it is orthorhombic (space group Pcab) [2, 3]. Although there have been various measurements of α-Mn₂O₃, including the heat capacity, magnetic susceptibility, x-ray diffraction and neutron diffraction, its magnetic properties are still under debate. The material shows an antiferromagnetic property below 80–90 K [4–8], but it appears that the spin ordering is not a simple antiferromagnet. The spins in the ordered state were reported to be noncollinear [6], but a more recent work claimed that the ordered spins are collinear at 10 K using a neutron diffraction experiment, suggesting a model of four sublattices [9]. Moreover, weak traces of additional magnetic phase transitions were found at 25 K [7] and 50 K [8].

In this work, we obtained the zero-field $^{55}$Mn nuclear magnetic resonance (NMR) spectra for α-Mn₂O₃ at the liquid helium temperature. The NMR experiment for magnetic materials can provide significant information pertaining to the ordered state, but there have been NMR experiments for α-Mn₂O₃ neither in an antiferromagnetic state nor in a paramagnetic state. The spectrum was measured in the low temperature range of 6–27 K, in which α-Mn₂O₃ is antiferromagnetic. From the results, we derived the magnetic moment of Mn³⁺ ions in α-Mn₂O₃ and the temperature dependence of the sublattice magnetization. The dipole field was calculated in order to explain the NMR spectral linewidth, and the spin–spin relaxation time was measured as a function of the frequency to investigate the effect of the Suhl–Nakamura interaction on the relaxation.

2. Experimental details

The sample was commercially available Mn₂O₃ polycrystalline powder of 99.999% purity (Sigma-Aldrich, Korea). Manganese sesquioxide exists in two forms, γ-Mn₂O₃ and mostly α-Mn₂O₃. We confirmed that the manganese sesquioxide used in the present study was purely α-phase within experimental error using x-ray powder diffraction. A closed-cycle cryogenic system was used to reach a low temperature. The $^{55}$Mn NMR spectra were obtained using a custom-built spectrometer. A conventional spin-echo pulse sequence ($90°−τ−180°$) was used, where the 90° pulse width was fixed at 2 µs during the entire measurement process. Given that the NMR resonance frequency for α-Mn₂O₃ is not known, we searched for the spectrum in the wide frequency range of 250–400 MHz, where the resonance signals of Mn³⁺ ions are usually found. For an accurate measurement, the probe coil was tuned and matched carefully at each frequency.

3. Results and discussion

The nuclei of the magnetic ions in magnetic materials such as Mn in α-Mn₂O₃ experience a strong hyperfine field, making it possible to obtain the NMR spectrum without an external
Figure 1. The $^{55}$Mn NMR spectra for $\alpha$-Mn$_2$O$_3$ over the temperature range of 6.7–27.4 K.

magnetic field. Figure 1 shows the zero-field $^{55}$Mn NMR spectra measured in the temperature range of 6.7–27.4 K. Above 27.4 K, the spin–spin relaxation time was too short to observe the echo signal. The spectrum is positioned around 314 MHz at the lowest measurement temperature. With an increasing temperature, the position of the spectrum shifted to the lower frequency side and the intensity decreased, whereas its shape remained mostly unchanged.

In a zero-field condition, the NMR resonance frequency for magnets is given by

$$\nu(T) = \frac{\gamma}{2\pi} (|A|\mu_T - H_{dip}),$$

where $A$ is the contact hyperfine coupling constant, $\mu_T$ is the electron magnetic moment at temperature $T$, $\gamma$ is the nuclei gyromagnetic ratio and $H_{dip}$ is the dipolar field generated by all neighboring magnetic moments. As a dipole field generated by an electron spin tends to be cancelled out by that of the neighboring spin pointing in the opposite direction, the sum of the dipolar hyperfine fields experienced by a nucleus is usually much weaker than the contact hyperfine field in antiferromagnets. Therefore, the resonance frequency in figure 1 is mostly determined by the contact hyperfine constant and the magnetic moment of the Mn ions.

In simple antiferromagnets, all of the nuclei of the magnetic ions are in equivalent positions and therefore experience the same dipolar field. Hence, the dipolar term in equation (1) simply induces an NMR frequency shift as an external magnetic field. According to a recent report [9], however, the magnetic structure of $\alpha$-Mn$_2$O$_3$ is not a simple antiferromagnet but is composed of four sublattices, each of which has a different type of antiferromagnetic order of the A, C, E or G type. Therefore, the dipolar field varies with the position of the Mn ions, and this generates not only a frequency shift but also spectrum broadening. We calculated the dipolar field that a nucleus experiences at each Mn$^{3+}$ ion site based on this model. As there are eight Mn ions in a unit defining one type, there could be a maximum of 32 different dipolar fields. Given that the differences of the lattice constants are only about 0.1% [3], the dipole fields were summed assuming cubic symmetry with a lattice constant of 9.4 Å from the nearest neighbors to the eighth, an addition that changed the result by a few per cent. The maximum value of the dipole field was about 4 MHz in frequency units, the average was −0.30 MHz and the dispersion was 1.5 MHz. The frequency shift due to the dipole field was only 0.1%, as expected. The
Figure 2. Temperature dependence of the local magnetization. The black solid circles are the experimental data of the NMR resonance frequency. The blue dashed line represents Bloch’s $T^2$ law and the red solid line represents equation (2) fitted to the data. Inset: $\nu(0) - \nu(T)$ versus temperature in the log–log scale.

broadening expected from the dispersion of the dipole field was 3 MHz, which is about half of the linewidth of the spectra in the figure. The dipole field is the main source of the broadening with quadrupole splitting. The distribution of the dipole field was not symmetric but weighed more on the negative side. This may be the reason for the slight asymmetry in the Gaussian shape of the spectrum.

Neglecting the dipole term, the NMR resonance frequency is proportional to the magnetic moment. Therefore, the decrease of the resonance frequency as the temperature increased represents the local magnetic moment being reduced by thermal fluctuation. Theory predicts $T^2$-dependence for the sublattice magnetization $M(T)$ of a simple antiferromagnet. There is a report claiming that $M(T)$ of $\alpha$-Mn$_2$O$_3$ actually follows $T^2$-dependence; however, no supporting data were presented [10]. However, the temperature dependence of the NMR resonance frequency in our data did not fit the $T^2$ law very well (blue dashed line in figure 2). An important reason for the deviation is the energy gap in the dispersion relation of the spin waves. At low temperatures, the magnetization of a ferromagnet or an antiferromagnet is mostly influenced by the long-wavelength spin waves. In contrast to a ferromagnet, there is a large energy gap in the dispersion relation of an antiferromagnet in the long-wavelength limit. Considering this energy gap ($E_g$), the sublattice magnetization of an antiferromagnet changes to [11]

$$M(0) - M(T) = a T^{3/2} \exp(-E_g/kT).$$

The graph plotted in the log–log scale in the inset clearly shows that equation (2) is a better fit to the data, especially at low temperatures, compared to the $T^2$ law. The large energy gap at a long wavelength in antiferromagnets is introduced by the interplay of anisotropy and the exchange energies; it is given by $E_g = (2E_A E_E)^{1/2}$, where $E_A$ and $E_E$ are the anisotropy and exchange energies, respectively. The initial energy gap in $\alpha$-Mn$_2$O$_3$ estimated by the fitting is 1.82 meV, which corresponds to the thermal energy at 21.0 K. By taking the Neel temperature
(90 K) as a measure of the exchange interaction, the anisotropy energy of $\alpha$-Mn$_2$O$_3$ is estimated to be about 2.5 K, or 0.22 meV. This energy gap is between those of the typical antiferromagnets with high and low anisotropy, FeF$_2$ and MnF$_2$, whose values are 76 and 12.6 K, respectively.

Extrapolation of the fitting curve to 0 K gives a resonance frequency of 314.3 MHz. This value added by the average dipole field, $-0.30$ MHz, should be identical to $(\gamma/2\pi)|A|\mu_0$ according to equation (1). The hyperfine coupling constant $|A|$ measured for Mn$^{3+}$ by ESR is 11.4 T per Bohr magneton [12]. The magnetic moment at zero temperature obtained from these relationships is $2.6\mu_B$ per Mn$^{3+}$ ion. This value is about 65% of the value of $4\mu_B$ as expected when only the spin contribution to the magnetic moment is considered. This indicates that the spin–orbit interaction due to the unquenched orbital angular momentum is strong in $\alpha$-Mn$_2$O$_3$. This value of the magnetic moment was used in the calculation of the dipole field above.

Figure 3(a) shows the $^{55}$Mn NMR spectra measured at the two different echo times ($2\tau$) of 60 and 120 $\mu$s. By increasing the echo time, it was noted that the central part of the spectrum decreases more than the other parts. In an ordered magnetic insulator containing a high concentration of identical magnetic nuclear spins, the Suhl–Nakamura (SN) interaction, in which nuclear spins are indirectly coupled by virtual magnons, plays a major role in the NMR relaxation at a low temperature. The interaction generates a frequency-dependent spin–spin relaxation time ($T_2$) with a minimum occurring in the center of the spectrum, as the majority of nuclear spins precess at this frequency. Therefore, the central part of the spectrum decays faster than the other parts as the echo time increases. The frequency dependence of the spin–spin relaxation time measured at 6.7 K in figure 3(b) actually shows that the relaxation rate ($1/T_2$) reaches its maximum around the center of the spectrum. The difference between the maximal and minimal values of $T_2$ is nearly 20%, which is small compared with the hundreds of percent found in some magnetic materials in which SN interaction is strong [13]–[15]. One of the reasons for this relatively weak SN interaction is believed to be the energy gap in the dispersion relation of the spin waves. SN interaction is more suppressed when the anisotropy energy associated with the energy gap is larger [16]. The linewidth of the spectrum is also broadened by the SN interaction. The linewidth due to SN interaction depends on the hyperfine
constant, exchange interaction and the anisotropy energy [11]. The linewidth calculated using these parameters for Mn$_2$O$_3$ is about 0.2 MHz. This is one order of magnitude smaller than the broadening observed in the spectrum in figure 1. SN interaction contributes little to the NMR spectral broadening for Mn$_2$O$_3$.

4. Conclusions

We measured the zero-field $^{55}$Mn NMR spectrum and its spin–spin relaxation time at low temperatures and calculated the dipolar hyperfine field for antiferromagnetic α-Mn$_2$O$_3$. The sublattice magnetization obtained quantitatively as a function of temperature from the spectra gave a magnetic moment of 2.6$\mu_B$ per Mn$^{3+}$ ion, an initial energy gap of 1.82 meV in the dispersion relation of the spin wave and an anisotropy energy of 0.22 meV. The magnetic moment is only 65% of the value of 4$\mu_B$, as expected when only the contribution of spin to the magnetic moment is considered. This indicates strong spin–orbit coupling between the localized spin and the unquenched orbital angular momentum. The anisotropy due to the spin–orbit coupling generated the large initial energy gap observed in the temperature dependence of the magnetization and suppressed the SN interaction, resulting in the weak frequency dependence of the spin–spin relaxation time. The dipole field calculation supports the collinear four-lattice model rather than the non-collinear single-lattice model, which predicts only the frequency shift but not the broadening in the spectrum.

Acknowledgments

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