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Magnetic state of $FeCl_3$ investigated by NMR

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ABSTRACT

The spin state of $FeCl_3$ was measured by Nuclear Magnetic Resonance (NMR) as a function of temperature and magnetic field. The sublattice magnetization obtained from the ^{57}Fe NMR spectrum fits well with the theoretical prediction for an antiferromagnet with a magnetic anisotropy field of less than 70 mT in the *ab*-plane. The field dependence of the ^{57}Fe NMR spectrum shows that a spin rotation plane of helical order starts to align perpendicularly to the external field direction as the field increases from 0 and ends around 4 T with no phase transition. From the spin tilting angle analysis, we obtained the quantitative relation among the exchange coupling constants.

1. Introduction

Magnetic systems having several different kinds of magnetic ions and/or competition among spin interactions frequently show canted spin order, frustration, or spin structure more complex than simple ferromagnets and antiferromagnets. It is difficult to understand its physical properties with simple theory or by the macroscopic measurement such as magnetization. Ferric chloride ($FeCl_3$) is one such complex magnetic system having helical spin order with an uncommon period of 15 [1]. Another interesting fact about $FeCl_3$ is that it was reported to undergo quantum phase transitions in magnetic field. $FeCl_3$ has a hexagonal layered crystal structure ($R\bar{3}$) that is isomorphic with BiI_3 and $CrBr_3$ [2,3]. Iron ions located at the center of the chlorine octahedron form honeycomb layers that are stacked up along the *c*-axis with a slight shift in the *ab*-plane direction so that every third layer ends up on top of the bottom one. $FeCl_3$ undergoes phase transition from paramagnetic to antiferromagnetic phase with decrease of temperature to around 9 K [4–10]. The antiferromagnetic phase is not a simple collinear type but a helical structure with its rotation axis along the $[14\bar{5}0]$ direction [1].

There was an interesting report that the spin structure of $FeCl_3$ changes in a magnetic field [4]. It was claimed that the spins have a double cone heliconical order instead of a 15 period helix in the ground state when an external magnetic field with its direction along the *c*-axis increases to over 1.5 T. The spins are canted from the *c*-axis by about 54°, and the projection of one spin to the axis is parallel while the other is antiparallel to the field. When the external field increases to over 4 T, the spin state changes once more to the so-called spin flop state, in which the spin direction is perpendicular to the magnetic field [11]. Supporting evidence for these results was found in the susceptibility measurement, which shows some changes around 1.5 T and 4 T. A change of the susceptibility near 1.5 T [5] is observed, but even near 20 K, which is well above the transition temperature. The change of susceptibility around 4 T [6] showed some characteristics of a first-order phase transition, but experimental evidence for the phase transition is not strong because the change was observed in a wide range of magnetic fields. The physics underlying these changes seems quite unclear.

In this work, we investigated the ground spin state of ferric chloride and the change of spin structure in the magnetic field using NMR. We obtained the magnetization curve of the sublattice by measuring the NMR frequency as a function of temperature; the results match well with the one expected for an antiferromagnet. The change of spin structure around the fields mentioned above was investigated from the distribution of spin canting angles obtained for various fields with NMR. Our results show no trace of phase transition in ferric chloride induced by the magnetic field. The coupling constants among the magnetic moments were estimated by measuring the spin tilting angles along strong magnetic fields.

2. Experiments

The sample used in the experiment is polycrystalline $FeCl_3$ of 99.99% purity (Sigma Aldrich Korea). Since ferric chloride absorbs moisture and rapidly changes, reacting with oxygen in the atmosphere, the sample was sealed in an NMR tube inside a glove-box filled with N_2 gas. A home-made spectrometer was used to measure the NMR spin echo using a $\pi/2-\tau-\pi$ pulse sequence in the temperature range from 1.7 K to 7 K. The tank circuit of the

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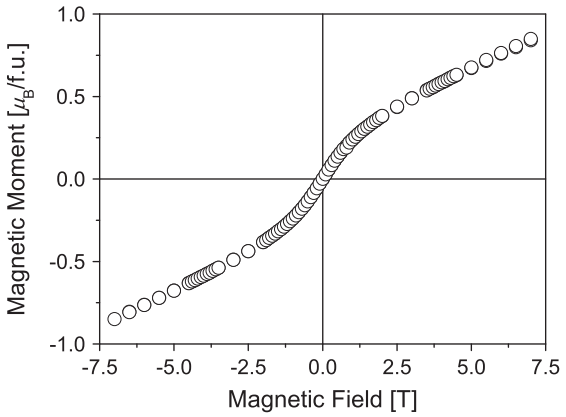

Fig. 1. Magnetization of polycrystalline $FeCl_3$ measured at 4 K.

NMR probe [12] was tuned to cover a frequency range from 25 MHz to 70 MHz. Magnetization was measured using a SQUID susceptometer at the Korea Basic Science Institute.

3. $M(H)$ and $M(T)$

Fig. 1 shows the $M(H)$ curve of $FeCl_3$ measured at 4 K in a magnetic field up to 7 T. The magnetization is much larger than that of simple antiferromagnets, though not as large as that of ferromagnets. Hysteresis was unobservable in this magnetic field range. Magnetization increases linearly with the field, but the rate decreases at around 1 T. This reminds us of the magnetic phase transition around 1.5 T, reported previously. However, around 4 T, at which point another magnetic phase transition was reported, no change was observed, at least in our polycrystalline sample.

The resonance frequency in the NMR experiment is proportional to the total magnetic field that a nucleus experiences. In magnetic materials, the total magnetic field is the vector sum of the external magnetic field and hyperfine field which ordered electron spins generate. Then, the resonance frequency of NMR f for magnetic materials is expressed as

$$f = \gamma |\vec{H}_{ext} + \vec{H}_{hyp}|, \tag{1}$$

where γ is the gyromagnetic ratio, and $\vec{H}_{ext}$ and $\vec{H}_{hyp}$ are the external and hyperfine magnetic fields, respectively. In zero magnetic field, the resonance frequency is proportional to the hyperfine field $\vec{H}_{hyp} = -A\langle\vec{\mu}\rangle$, where $\langle\vec{\mu}\rangle$ is the thermal average of the magnetic moment of an electron and A is the hyperfine coupling constant. Therefore, the temperature dependence of the resonance frequency for a magnetic material measured in zero field is proportional to $\langle\vec{\mu}\rangle$, which is the same as $M(T)$ for ferromagnets.

Fig. 2(a) shows the NMR spectrum of $FeCl_3$ observed in zero magnetic field. Multiple peaks are observed in the range from 28 MHz to 47 MHz, and, apart from that, one peak is observed at around 64 MHz. The multiple peaks in the low frequency region are generated by chlorine nuclei; the single peak around 64 MHz is generated by iron nuclei [7]. Chlorine exists in two different isotopes, ^{35}Cl and ^{37}Cl, with a population ratio of 3:1 in nature. Since their gyromagnetic ratios are different, at 4.18 and 3.48 MHz/T, respectively, their NMR spectra are expected to appear separated. The nuclear spins of chlorine isotopes are 3/2, and therefore, nuclear quadrupole splitting occurs. Chlorine ions are not magnetic but their nuclei experience a transferred hyperfine field from neighboring iron ions. Chlorine ions can be in three different environments according to their relation with iron ions. Consequently, there can be, at most, 18 different peaks, and this is why multiple peaks are observed in a wide range.

We measured the resonance frequency of the ^{57}Fe NMR signal for various temperatures below the phase transition temperature. The resonance frequency decreases as the temperature increases, as shown in Fig. 2(b). A hyperfine field, obtained by extrapolation of the graph to 0 K had a value of 49.6 T, which is consistent with the result of a previous Mössbauer work [4]. For the iron magnetic moment of $4.3\mu_B$ [1], the hyperfine coupling constant A is estimated at 11.4 T/μ_B. This constant is independent of temperature, and therefore, the temperature dependence of the hyperfine field is attributed to that of the electron magnetic moment. Magnetization decay due to spin wave excitation, $\Delta M(T) = M(0) - M(T)$, is proportional to $T^{3/2}$ for a ferromagnet and to T^2 for an antiferromagnet [13]. These theoretical predictions fit the experimental data; they are plotted together in Fig. 2(b). The graph clearly shows that the T^2 law fits the data much better than does the $T^{3/2}$ law.

Bloch's $T^{3/2}$ and T^2 laws are applicable when the energy gap is absent in the spin wave excitation. The excellent fit of the T^2 law to our data means that the energy gap in the spin wave of the antiferromagnetic ferric chloride is small. The energy gap makes $\Delta M(T)$ changes with temperature as $\Delta M(T) \propto \exp(-E_G/kT)T^{3/2}$. The energy gap is given by $E_G = \sqrt{2E_{exc}E_{ani}}$ for antiferromagnets, where E_{exc} and E_{ani} are the exchange and magnetic anisotropy energies, respectively. Fitting this formula to our data yields an energy gap of 2 K in Kelvin temperature. Taking the exchange energy as roughly equal to the transition temperature, 10 K, the anisotropy energy is estimated to be about 0.1 K. This anisotropy energy corresponds to 70 mT, which should be the magnetic anisotropy field in the *ab*-plane [7]. This is one order of magnitude smaller than the value when the anisotropy is measured perpendicular to the plane, for which the value was estimated to be 800 mT [4].

4. Magnetic field dependence

According to Eq. (1), the angle between the hyperfine and the external fields can be obtained from the resonance frequency measured in the external field. The hyperfine field of an iron ion in ferric chloride is antiparallel to the magnetic moment; therefore, the canting angle of the magnetic moment of an iron ion from the external field is obtained from the NMR experiment in the field. If a single crystal is used in the experiment, a shift of resonance peak is expected by the increase in the field. When a polycrystalline sample is used, as our experiment, the angle is randomly distributed and the resonance peak broadens instead of shifting.

Fig. 3(a) shows the NMR spectra of ferric chloride obtained in various magnetic fields from 0 to 7 T. The peak frequency and the line width vs. the field are plotted in Fig. 3(b) where the bar passing through each data point represents the Full Width Half Maximum (FWHM) of the spectrum. The resonance peak broadens and shifts to the high frequency side as the field increases from 0 T. Above 3 T, the line width becomes narrower and the center frequency of the signal shifts to the lower frequency side with the increasing field.

The previous report of Mössbauer work claimed that the spins are ordered to have two different directions, whose projections to the field direction are antiparallel to each other when the external magnetic field, with its direction along the *c*-axis, is between 1.5 T and 4 T. If spins align in this way, it is expected that two different spin directions will also be observed for polycrystalline samples because the external field is large enough to overcome the anisotropy field [4,7]. In our NMR spectra, no abrupt change is observed around 1.5 T or 4 T. There is a slight change of slope in magnetization (Fig. 1) around 1 T, but this is due to the anisotropy field along the vertical direction [4]. Therefore, there is no trace of the phase transitions from the helical order to the heliconical order with two different spin directions, or from the heliconical