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Magnetic properties of MnF_3 investigated by ^{55}Mn NMR and M (H) measurement

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ABSTRACT

The $M(T)$ and $M(H)$ curves were measured to study the spin-ordered state in MnF_3 at low temperatures. In order to obtain the temperature dependence of magnetization, Mn^{3+} NMR resonance frequency was measured as a function of temperature. The resulting curve fits well to the initial temperature dependence of the magnetization expected for antiferromagnets with magnetic anisotropy, $T^{3/2}\exp(-E_G/k_BT)$, with an energy gap E_G of about 30 K. From the comparison of the $M(H)$ curve and classical theory, the relation between the anisotropy energy, K_a, and the exchange coupling constant between the nearest neighbors, J_1, was found to be $K_a \sim -1.8J_1 + 9.8$ in the absolute temperature unit.

1. Introduction

Manganese trifluorides(MnF_3) is one of the antiferromagnets whose magnetic structure is well understood from the indirect exchange interactions predicted in a given crystal structure. The fluorine octahedron surrounding a Mn ion at its center is distorted by the Jahn-Teller effect because Mn^{3+} ions have 4 electrons in the 3d orbital in contrast with Cr^{3+} ions in CrF_3 and Fe^{3+} ions in FeF_3 having 3 and 5 electrons, respectively. The distortion generates an orbital order in Mn ions and makes the MnF_6 octahedra have three different bond lengths between the Mn and F ions, resulting in a monoclinic crystal structure [1] with 12 molecules per unit cell. The A-type antiferromagnetic spin order of MnF_3 ($T_N = 43$ K) is, however, described well in an idealized cubic form [2].

One of the most interesting physical properties of MnF_3 resulting from the spin order is the negative thermal expansion (NTE) observed at low temperatures [3]. The volumetric thermal expansion coefficient of MnF_3 is large and negative ($-120 \times 10^{-6}\,K^{-1}$) in the range from 20 K to the Neel temperature. The Jahn-Teller distortion observed in MnF_3 at low temperatures remains even above room temperature until the material decomposes into MnF_2 by heating [4]. Therefore, the NTE of MnF_3 is not related to the orbital order but the spin order. The NTE due to the spin order is already known through the study of invar alloy but is rarely found in the fluorides [5], and the expansion coefficient of MnF_3 is large enough to attract attention. The NTE in invar alloy is relatively well understood through arguments over the past century [6], but that in MnF_3 is the subject under investigation.

It is necessary to know the details of the interactions generating the spin structure such as exchange, anisotropy and magnitude of the spin, in order to understand the NTE of MnF_3. In this study, we obtained the $M(T)$ and $M(H)$ curves of MnF_3 by NMR and SQUID measurements. It is difficult to obtain the $M(T)$ curve for an antiferromagnet with a magnetometer. The NMR frequency in zero external magnetic field is proportional to the magnetic moment of a magnetic ion. The temperature dependence of the resonance frequency of Mn^{3+} ions was measured below the Neel temperature in order to obtain the M(T) curve. The NMR spectrum was searched carefully in a wide frequency range to check for the coexistence of two different magnetic phases predicted in the 2γ state model explaining the NTE qualitatively [7]. The spin wave energy gap was obtained from the comparison of theory with the measured $M(T)$ curve. The nearest neighbor exchange constant and the magnetic anisotropy constant were estimated by comparing the $M(H)$ curve with a classical model.

2. Experiment

The MnF_3 sample was a powder with 99.9% purity purchased from Sigma-Aldrich Korea. The sample was put into a 5 mm NMR tube and sealed carefully in a glove box to avoid hydrolyzation into HF in a moist environment. The NMR echo signal was obtained by using the conventional 90°–τ–180° pulse sequence. The ^{55}Mn NMR

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signal was searched for in the frequency range from 50 to 320 MHz below the Neel temperature. The $M(H)$ curves were measured by a SQUID magnetometer.

3. Results and discussion

The local field a nucleus of a magnetic ion experiences is usually the hyperfine field due to the magnetic moment of its own atom. The magnitude of the hyperfine field is proportional to the thermally averaged magnetic moment, and the direction is commonly opposite to that of the magnetic moment. The resonance frequency of NMR is proportional to the local field induced at the nuclei and therefore, proportional to the magnetic moment for magnetic materials. Fig. 1(a) shows the spectra of ^{55}Mn NMR for MnF_3 obtained at various temperatures below the Neel temperature. Only one single peak with a linewidth of about 2 MHz was observed at a given temperature. The observation of one single peak implies that all the Mn ions in MnF_3 are in the same valence state. That is, the whole sample is in the chemically homogeneous phase, where all the Mn ions are in the same chemical and electronic environment.

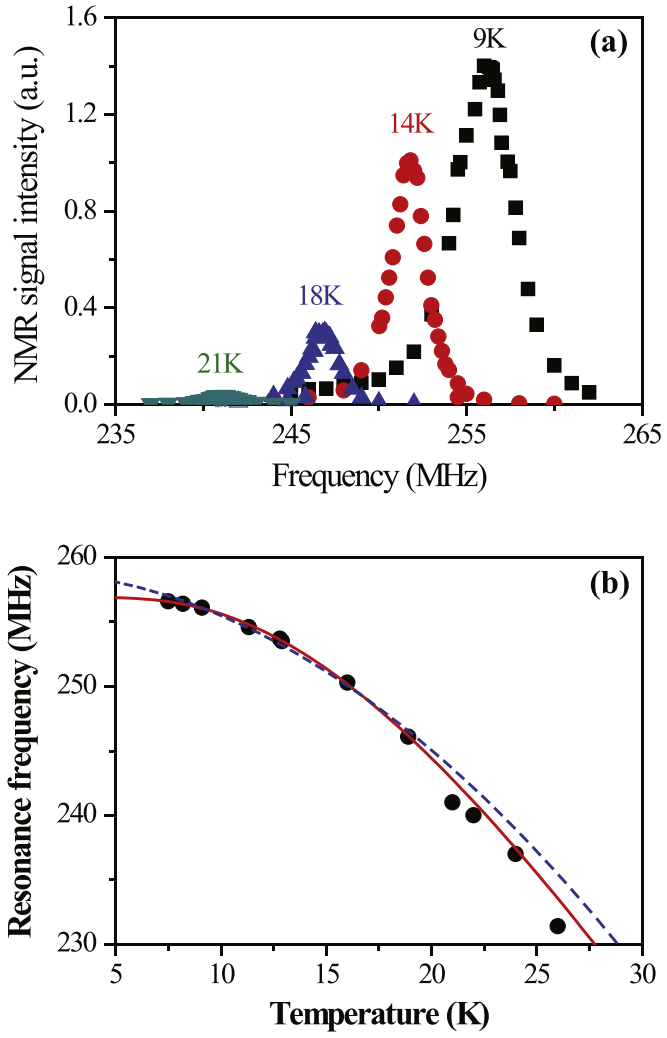

Fig. 1. (a) The Mn^{3+} NMR spectra for MnF_3 obtained at various temperatures below the Neel temperature. (b) Temperature dependence of the NMR resonance frequency of MnF_3. The solid circles are the experimental data, and the red solid and blue dashed lines represent $T^{3/2}\exp(-E_G/k_BT)$ and T^2, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In the 2γ state model developed by Weiss to explain the invar effect, a ferromagnetic phase having large unit cell volume is mixed in an antiferromagnetic phase having small unit cell volume. As temperature increases, the antiferromagnetic phase becomes more energetically stable and the sample volume decreases. This model explains the NTE phenomenologically, but experimental evidence has not been observed. Our NMR spectrum provides evidence that there are no two different spin ordered phases mixed with each other in MnF_3. The mixed phase assumed in the 2γ state model can be not only a mixture of the magnetic states having different spin orders such as ferromagnetic and antiferromagnetic phases, but also the magnetic states with different magnetic moments such as high and low spin states. The expected total spin values of four 3d electrons in a Mn^{3+} ion are 2, 1, or 0. The NMR spectrum of the Mn^{3+} ion whose spin state is 2 used to be observed in the range of 200–300 MHz. Because the NMR spectrum of MnF_3 is observed in this range, the spin state of the Mn^{3+} ions in MnF_3 is concluded to be 2. The NMR spectrum was searched for in the wide frequency range of 50–320 MHz, but no other peak was observed. There is no evidence for the existence of the low spin state mixed with the high spin state in MnF_3.

Fig. 1(b) shows the temperature dependence of the resonance frequency below the Neel temperature. Extrapolation to 0 K yields a resonance frequency of 257 MHz, which corresponds to the hyperfine field of 24.3 T. When the excitation of a spin wave, of arbitrary wave vector k, corresponds to decreasing the total S_z by $\hbar$, the magnetization varies as $T^{3/n}$ for a dispersion relation $\omega \sim k^n$ [8]. This is true for a ferromagnet and leads to the Bloch's $T^{3/2}$ law but not for an antiferromagnet. A correct counting of the total number of spin waves predicts that the initial decrease of the sublattice magnetization of antiferromagnets is proportional to T^2, or $T^{3/2}\exp(-E_G/k_BT)$, where E_G is the energy gap of the spin wave if the effect of the magnetic anisotropy is considered [9]. The fitting curves of the two cases are also plotted together in the figure. The formula considering the magnetic anisotropy fits better to the data and the energy gap obtained from the fit is 30 ± 5 K.

Fig. 2 shows the $M(H)$ curve of the MnF_3 obtained in the range from 0 T to 7 T at 30 K. The magnetization increases almost linearly with the external field. The $M(H)$ curve obtained at 4 K is similar but shows a weak ferromagnetic behavior; that is, the magnetization rises fast below 2 T, above which it increases linearly. In the linear region, the magnetization curve obtained at 4 K is parallel with that obtained at 30 K. This weak ferromagnetic

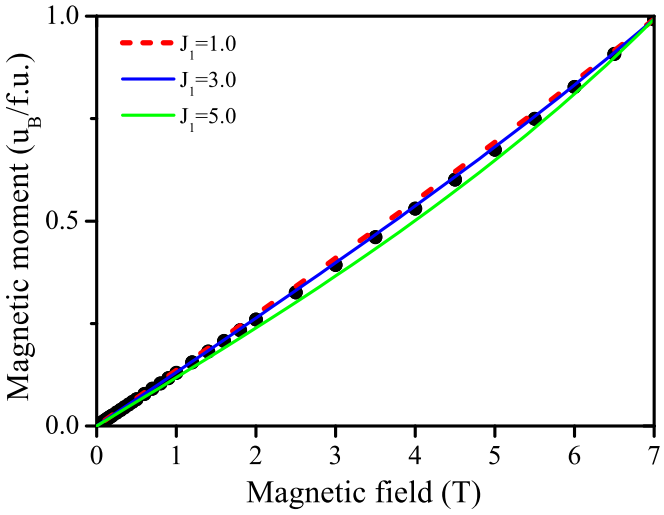

Fig. 2. The $M(H)$ curve of MnF_3. The solid symbols represent the experimental data obtained at 30 K, and the lines are the theoretical curves expected for various J_1 values.