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NMR observation of field-induced domain reorientation in antiferromagnetic $KNiF_3$

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It is shown that the process of field-induced domain reorientation that takes place in cubic antiferromagnets strongly affects the ^{19}F NMR line shape of the nearly isotropic cubic antiferromagnet $KNiF_3$.

I. INTRODUCTION

In uniaxial two-sublattice antiferromagnets it is well known that a sharp transition to a "spin-flop" (SF) phase takes place at a critical field $H_{cr} = (2H_A H_E)^{1/2}$, where H_A and H_E are anisotropy and exchange fields, respectively ($H_E >> H_A$). In cubic antiferromagnets however, the situation is quite different. In the absence of an applied magnetic field a domain structure must exist such that the sublattice magnetization within each type of domain is oriented with equal probability along any axis of a set of fourfold axes of the crystal.[1] The application of a magnetic field causes domain-wall movement and different configurations are possible depending upon the direction and strength of the applied field $\vec{H}_0$. As the field is increased, domain reorientation can take place towards a configuration where the sublattice magnetizations are preferentially aligned perpendicular to the applied field with a small tilt towards $\vec{H}_0$ by an angle $\theta = \arcsin(H_0/2H_E)$. Such a "domain flopping" however, can be completed in a cubic antiferromagnet at field strengths considerably smaller[2-5] than the critical field H_{cr} and can also differ from the sharp SF transition in uniaxial systems in other important aspects.

Although the existence of antiferromagnetic domains and their general behavior in an applied field have been predicted some time ago,[6] the details of AF-SF domain configurations in cubic[2] as well as uniaxial[7] systems have been subject to careful experimental study only recently. The purpose of this paper is to illustrate the effect of field-induced domain reorientation upon the nuclear magnetic resonance of a cubic antiferromagnet.

In the case of $KNiF_3$ there is also a different reason to inquire about the AF-SF domain structure. $KNiF_3$ is a nearly isotropic antiferromagnet with $H_A/H_E \sim 7 \times 10^{-5}$. For a fully isotropic three-dimensional antiferromagnet it has been shown by Fisher, Nelson, and Kosterlitz[8] that the field dependence of the ordering temperature should be markedly different from the mean-field prediction. Such behavior has recently been confirmed experimentally[5] in $KNiF_3$ for fields large enough such that the crystal contained predominantly "perpendicular" domains. For lower fields however, Petit, Ferré, and Nouet[2] have concluded from magnetic circular dichroism measurements that "parallel" domains prevail over perpendicular ones for $\vec{H}_0 \parallel [001]$. If a single domain crystal with the sublattice magnetization parallel to $\vec{H}_0$ could be obtained, measurements of the ordering temperature as a function of magnetic field could clarify the magnetic phase diagram of $KNiF_3$.

The two classic examples of antiferromagnets that remain basically cubic at temperatures well below the ordering temperature T_N are $RbMnF_3$ and $KNiF_3$. In zero applied field, four types of equivalent domains with their sublattice magnetizations along the body diagonals of the cube exist in $RbMnF_3$. With a magnetic field applied along a [001] axis, domain reorientation takes place giving rise to a configuration of two types of perpendicular domains[4] at fields somewhat smaller than $H_{cr} = 2.7$ kOe. In $KNiF_3$, a rather different behavior has been observed.[2,3] Three types of domains have been identified with their sublattice magnetizations respectively oriented along [100] (d_x domains), [010] (d_y domains), and [001] (d_z domains). Application of a magnetic field along [001] leads to the complete extinction of d_z domains at field strengths H_{df}, reportedly dependent upon sample size. Values of H_{df} between 8 and 20 kOe, much smaller than $H_{cr} = 44$ kOe, have been observed[2] in $KNiF_3$ crystals of various sizes. Moreover a threshold field also appears to exist below which no domain-wall motion takes place. In this low-field region the volume fraction of d_z-type domains has been inferred[2] to be considerably larger than that of perpendicular domains. It is worth pointing out however that some of the above observations are not well understood. For a perfectly cubic, strain-free crystal, one would expect to find in zero-field domains of d_x-, d_y-, or d_z-type with equal probabilities. Neither is it clear from a microscopic point of view, what

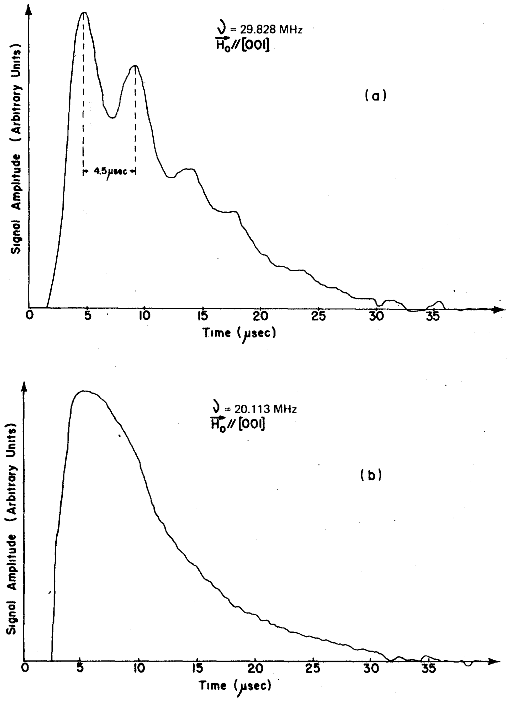

FIG. 1. (a) ^{19}F free-induction-decay signal in antiferromagnetic KNiF$_3$ at $T = 10$ K for $\vec{H}_0 \parallel [001]$ and frequency $\nu = 29.828$ MHz. (b) ^{19}F FID signal in KNiF$_3$ under identical conditions as in (a) except that the frequency is $\nu = 20.113$ MHz.

would be the origin of the threshold field for domain-wall motion in KNiF$_3$.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The effect of field-induced domain reorientation upon the nuclear magnetic resonance of KNiF$_3$ was examined using a conventional pulsed NMR spectrometer to detect ^{19}F free-induction decay (FID) signals in KNiF$_3$. The crystal had the shape of a parallelepiped of size $5 \times 6 \times 7$ mm^3 and was oriented by x-rays with a [001] axis parallel to the external field. In the temperature range $10 \leq T \leq 78$ K no observable change in the FID signals was detected at constant magnetic field. The ^{19}F spin-lattice relaxation time[9] however varied over three orders of magnitude in this range of temperatures.

Figure 1(a) shows a ^{19}F FID signal in KNiF$_3$ at $T = 10$ K. The frequency was $\nu = 29.828$ MHz and a magnetic field $H_0 = 7415$ Oe was applied along a [001] axis. The FID exhibits a periodic pattern of period $\tau = 4.5 \pm 0.3$ μsec and corresponds to the Fourier transform of a spectrum of two resolved lines separated by a splitting

$$(\Delta H)_{\text{exptal}} = H_0/\nu\tau = 55.3 \pm 4 \text{ Oe} . \tag{1}$$

A rather dramatic change occurs in the FID when the magnetic field is decreased by only 30%. A mere reduction of the splitting by this amount would have still produced a clearly observable periodic pattern of period $\tau = 6.2$ μsec. However a quite different behavior is observed. Figure 1(b) shows a FID signal obtained under the same conditions as in Fig. 1(a), except that the frequency has been reduced to $\nu = 20.113$ MHz. The periodic pattern of Fig. 1(a) is no longer detectable in the FID of Fig. 1(b) which appears to correspond to a single line. This line is homogeneously broadened as evidenced by the absence of a spin-echo signal following a 90-180° pulse sequence. The fact that no additional broadening is observed in Fig. 1(b) and that no spin-echo signal is detected seems to confirm that this line is largely a single line rather than a merger of several lines.

At $T > T_N = 246$ K the observed FID signals for $\vec{H}_0 \parallel [001]$ correspond to the known spectrum of two lines reported[10] for KNiF$_3$ in the paramagnetic phase. In the higher frequency ($\nu = 29.828$ MHz) case, the only observable change in the paramagnetic phase is a slight modification in the shape of the decay which becomes exponential while the periodic pattern remains practically unchanged. At the lower frequency ($\nu = 20.113$ MHz) however, the periodic pattern absent in the antiferromagnetic phase is present, as expected in the paramagnetic phase with a proportionally larger period $\tau = 6.2 \pm 0.5$ μsec.

One can understand the above results for $T < T_N$ as being a consequence of the reorientation of domains under the applied field. For a configuration where d_x-, d_y-, and d_z-type domains coexist one should expect in principle four NMR lines for $\vec{H}_0 \parallel [001]$. The origin of these lines can be simply understood in the following manner. In each type of domain two nonequivalent fluorine sites exist in the cubic perovskite structure with the F-Ni internuclear vector either parallel ("parallel sites") or perpendicular ("perpendicular sites") to $\vec{H}_0$. In addition, fluorines in d_z domains also have different Larmor frequencies from fluorines in d_x and d_y domains because of the considerable difference between the values of the parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) electronic susceptibilities in the antiferromagnetic phase at low temperatures.[11] This gives in principle a total of four lines.

The shift between the different lines arises from the hyperfine interaction between each fluorine and its two neighboring Ni^{2+} ions in different sublattices, as well as from the dipolar interaction between the fluorine nuclear magnetic moment and the magnetic moments of the Ni^{2+} ions. A simple adaptation of the calculations valid for the paramagnetic case[10] yields the following shifts:

$$(2\pi\nu/\gamma_n - H_{\parallel}^{xy})/H_{\parallel}^{xy} = 2A_{\parallel}\chi_{\perp}/Ng\mu_{\mathrm{B}}\hbar\gamma_n + \chi_{\perp}S_{\parallel}^{D}/N , \tag{2a}$$

$$(2\pi\nu/\gamma_n - H_{\perp}^{xy})/H_{\perp}^{xy} = 2A_{\perp}\chi_{\perp}/Ng\mu_{\mathrm{B}}\hbar\gamma_n - \chi_{\perp}S_{\parallel}^{D}/2N\ , \tag{2b}$$

$$(2\pi\nu/\gamma_n - H_{\parallel}^{z})/H_{\parallel}^{z} = 2A_{\parallel}\chi_{\parallel}/Ng\mu_{\mathrm{B}}\hbar\gamma_n + \chi_{\parallel}S_{\parallel}^{D}/N\ , \tag{2c}$$

$$(2\pi\nu/\gamma_n - H_{\perp}^{z})/H_{\perp}^{z} = 2A_{\perp}\chi_{\parallel}/Ng\mu_{\mathrm{B}}\hbar\gamma_n - \chi_{\parallel}S_{\parallel}^{D}/2N\ . \tag{2d}$$

Where $H_{\parallel}$, $H_{\perp}$ refer to resonance fields at frequency ν for parallel and perpendicular sites, whereas H^z, H^{xy} denote resonance fields for d_z and d_x, d_y domains, respectively. $A_{\parallel}$ and $A_{\perp}$ in Eqs. (2) are components of the hyperfine tensor in the local coordinate system.[12] $S_{\parallel}^{D}$ is a dipolar sum for parallel fluorine sites, N is Avogadro's number, g is the Ni^{2+} g factor, γ_n is the $^{19}\mathrm{F}$ gyromagnetic ratio, and μ_{B} is the Bohr magneton.

Equations (2c)-(2d) imply that the resonance shifts for d_z domains are proportional to the parallel molar electronic susceptibility $\chi_{\parallel}$. Typical values of $\chi_{\parallel}$ in antiferromagnets[11] for $T << T_N$ indicate however, that $H_{\parallel}^{z} - H_{\perp}^{z}$ should be much smaller than the resonance linewidth of each line. Thus for fluorine nuclei in d_z-type domains one expects a single line at the undisplaced field $2\pi\nu/\gamma_n$ as observed in our $\mathrm{KNiF_3}$ sample for $H_0 \approx 5$ kOe [Fig. 1(b)]. In domains of d_x-, and d_y-type however, the sublattice magnetizations are canted. The corresponding shifts in Eqs. (2a) and (2b) are proportional to $\chi_{\perp}$ which is comparatively large and temperature independent. Thus for a crystal containing only perpendicular domains one expects a spectrum of only two lines as observed for $\nu = 29.828$ MHz [Fig. 1(a)]. Moreover the shift between both lines is given to a very good approximation by

$$H_{\perp}^{xy} - H_{\parallel}^{xy} = \frac{2\pi\nu\chi_{\perp}}{\gamma_n}\left(\frac{2(A_{\parallel}-A_{\perp})}{Ng\mu_{\mathrm{B}}\hbar\gamma_n} + \frac{3S_{\parallel}^{D}}{2N}\right)\ . \tag{3}$$

Substituting into Eq. (3) the following numerical values obtained from Ref. 10:

$$g = 2.28\ ,\quad A_{\perp} = 25.1\times 10^{-4}\ \mathrm{cm}^{-1}\ ,$$

$$A_{\parallel} = 51.5\times 10^{-4}\ \mathrm{cm}^{-1}\ ,$$

$$S_{\parallel}^{D} = \left(\sum_i \frac{1}{r_i^3}(3\cos^2\theta_i - 1)\right)_{\parallel} = 5.636\times 10^{23}\ \mathrm{cm}^{-3}$$

(corrected for nonspherical Ni^{2+} ions), yields for $\nu = 29.828$ MHz,

$$H_{\parallel}^{xy} - H_{\perp}^{xy} = 58.9\ \mathrm{Oe}\ , \tag{4}$$

in good agreement with $(\Delta H)_{\mathrm{expt}}$. A value

$$\chi_{\perp} = 1.755\times 10^{-3}\ \mathrm{cm^3/mole}$$

corresponding to the measured [13] susceptibility at the Néel temperature corrected for orbital contributions[10] was used in Eq. (3).

From this discussion we are led to the conclusion that domain reorientation has indeed taken place in our $\mathrm{KNiF_3}$ crystal as the magnetic field, parallel to [001], was decreased from $H_0 \approx 7,4$ kOe to $H_0 \approx 5$ kOe with a large reduction of d_x and d_y domains in favor of d_z domains. The existence of a single line at low fields would also confirm the presence of a comparatively large volume fraction of parallel domains as was suggested in Ref. 2. It is also apparent that AF-SF domain structure can have a considerable effect upon the nuclear resonance of a cubic antiferromagnet and must probably be taken into account in any detailed study of the NMR line shape or the spin-lattice relaxation mechanism in these systems.

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