DIRECT DETECTION OF F^{19} NUCLEAR ACOUSTIC RESONANCE IN ANTIFERROMAGNETIC $RbMnF_3$ †

R. L. Melcher* and D. I. Bolef
Arthur H. Compton Laboratory of Physics, Washington University, Saint Louis, Missouri

and

R. W. H. Stevenson
Department of Natural Philosophy, University of Aberdeen, Aberdeen, Scotland
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The direct detection of the resonant absorption of energy from ultrasonic waves by nuclear spin systems,[1] nuclear acoustic resonance (NAR), previously has been limited to nuclei with spin $I>\frac{1}{2}$, in which cases the dynamic nuclear quadrupolar interaction has been responsible for the nuclear spin-acoustic phonon coupling. Other coupling mechanisms have been proposed. Silverstein[2] suggested that in antiferromagnetically ordered materials a two-step process involving the magnetoelastic excitation of a virtual magnon state, which in turn is coupled through the hyperfine interaction to the nuclear spin system, would be an effective mechanism for coupling acoustic waves to nuclear spins. Direct modulation of the hyperfine interaction between the magnetic moment of a magnetic ion and the nuclear spin of a neighboring nonmagnetic ion was proposed by Buishvili and Giorgadze[3] as a mechanism for coupling ultrasonic waves to nuclear spins in magnetic crystals.

By use of a pulse-saturation technique at 4.2°K, Denison et al.[4] reported that they were able to saturate the conventional F^{19} NMR line by irradiating a sample of the canted antiferromagnet $KMnF_3$ with ultrasound at the nuclear Larmor frequency. Since F^{19} has spin $\frac{1}{2}$, they interpreted their results as being evidence of an acoustic coupling via modulation of the hyperfine interaction between the Mn^{++} ion and the F^{19} nucleus. Walther[5] recently reported the observation, using pulse techniques, of an anomalous absorption of ultrasound as a function of temperature in antiferromagnetic MnTe which he proposed was due to coupling of the ultrasound to the Mn^{55} ($I=\frac{5}{2}$) nucleus.

$RbMnF_3$ is a simple antiferromagnet with the cubic perovskite structure at all temperatures. Because of its convenient Néel temperature ($T_N=83$°K) and low magnetic anisotropy it has been studied in detail by a variety of techniques.[6-8]

We have succeeded in detecting directly the increase in ultrasonic attenuation as the externally applied magnetic field was swept through the value corresponding to the F^{19} nuclear resonance in a single crystal of antiferromagnetic $RbMnF_3$. The cw marginal-oscillator technique used enables one to display the NAR absorption line on a strip-chart recorder.[1] The coupling of energy to the F^{19} nuclear spin system from longitudinal ultrasonic waves propagating along the [100] axis was measured as a function of direction of applied field, frequency, acoustic power, and temperature. Separate measurements were made of the conventional NMR absorption in a second crystal of $RbMnF_3$.

The F^{19} NAR absorption was observed at two frequencies ($\nu_1=11.518$ MHz and $\nu_2=12.155$ MHz) and in each case the resonant magnetic field for the stronger of the two fluorine lines at 77.4°K ($H_{01}=2790$ Oe and $H_{02}=2940$ Oe) corresponded to the F^{19} gyromagnetic ratio if account is taken of a shift, $\Delta H/H_0=0.033\pm0.001$, in the resonant field. The observed shift agreed with that measured by conventional NMR. The shift is due to the hyperfine interaction of the F^{19} nucleus with the magnetic moment of neighboring Mn^{++} ions.[9] Because $RbMnF_3$ remains cubic below the Néel temperature and because each F^- ion has one Mn^{++} ion neighbor on each of the two magnetic sublattices, in zero applied field there is no resultant static hyperfine field at the F^{19} nucleus. This is in contrast to other less symmetric antiferromagnets, e.g., F^{19} in $KMnF_3$ and MnF_2. On application of an external field the Mn^{++} moments become slightly polarized in the direction of the field regardless of the magnetic sublattice on which they reside. This produces a static hyperfine field at the fluorine nuclei in the direction of the applied field and a resulting increase in nuclear resonance frequency. For an arbitrarily oriented external field there are three inequivalent F^{19} sites; two or three of these sites become equivalent when the field is aligned along certain symmetry directions.

Saturation measurements were made at 77.4

and 68.5°K with $\vec{H}_0$ parallel to the [010] axis and perpendicular to the direction of propagation of the acoustic waves (propagation vector $\vec{k} \parallel [100]$). For a fixed voltage $V_T = 100$ mV peak to peak applied across the quartz transducer, the NAR line at 77.4°K was 7-12% saturated, whereas at 68.5°K the line was 20-25% saturated. The best signal-to-noise ratio ($S/N \simeq 100$ for 1-sec time constant) was obtained for $V_T = 100$ mV; the data reported here were all taken with this value of V_T.

Figure 1 shows a recorder trace of the NAR spectrum at 80°K and $\theta = \sphericalangle(\vec{H}_0, \vec{k}) = 90°$. The spectrum (which, due to the magnetic field modulation and synchronous detection technique used, is shown in Fig. 1 as the first derivative of the absorption) consists of two narrow (linewidth = 14 Oe) overlapping lines superimposed on a broad (linewidth $\simeq 250$ Oe) absorption which itself shows some structure. Both the broad and narrow sets of lines showed similar saturation characteristics and similar angular behavior. The two sets of lines behaved differently with respect to their temperature dependence; the narrower lines showed no measureable shift in magnetic field at fixed frequency as the temperature was lowered from 82 to 54°K, whereas the broad spectrum shifted to lower field values as the temperature was lowered. The total change in position from 82 to 65°K was about 450 Oe for the broad spectrum.

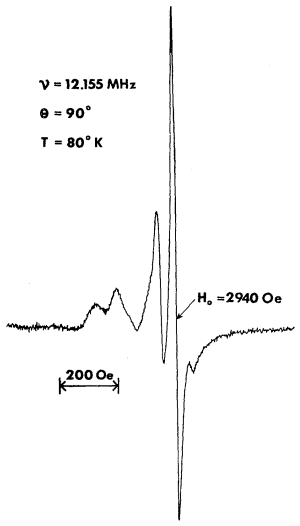

FIG. 1. Recorder tracing of the derivative of the F^{19} NAR spectrum in $RbMnF_3$ with $\vec{H}_0 \parallel [010]$ and $\vec{k} \parallel [100]$. $V_T = 100$ mV peak to peak. $\theta = \sphericalangle(\vec{H}_0, \vec{k})$. Integrating time $\tau = 0.1$ sec. Magnetic field increases from left to right.

We do not know the origin of the broad line spectrum although it appears to be a resonant absorption in which a temperature-dependent internal field adds to the applied external field to satisfy a resonance condition. The remainder of this report refers to the narrow line spectrum.

The narrow, two-line spectrum is identified conclusively with the F^{19} NAR. With an external field applied along the [010] axis there are two inequivalent F^{19} nuclear sites, one of which contains twice the number of nuclei as the other. This results in a two-line spectrum whose relative intensities are 2:1. The positions in field of the observed narrow acoustic resonances coincide with those observed by conventional NMR techniques at the same frequency and temperature in a $RbMnF_3$ sample of similar origin. In order to disentangle the overlapping NAR spectrum, efforts are underway to go to higher magnetic fields.

The angular dependence of the signal strength as the magnetic field was rotated in the (001) plane is shown in Fig. 2. This curve is symmetric with respect to and very sharply peaked at $\theta = 90°$, and shows a small but definitely discernible signal remaining at $\theta = 0°$. Several factors prevent a quantitative measure of the exact angular behavior of the interaction strength. Because of the inequivalent nuclear sites, the number of fluorine nuclei contributing to a given resonance line varies as a function of angle. In addition to the intrusion of the broad line spectrum mentioned above, there exist in this material strong magnetoelastic effects caused by the rotation of the sublattice magnetization away from the direction of the applied field. A preliminary report of this nonresonant magnetic-field-dependent ultrasonic velocity and attenuation has been published and is being studied further.[10] This effect causes the appearance for $\theta \neq 90°, 0°$ of broad, nonresonant attenuation changes which make quantitative measurements of the NAR signal strength very difficult. At higher magnetic fields the sublattice magnetizations are essentially perpendicular to the applied magnetic field at all angles and one thus avoids these background attenuation effects. The misorientation of the (001) crystalline plane with respect to the plane of the magnetic field was known to be less than 2°.

Figure 3 shows the temperature dependence of the NAR signal strength for $\theta = 90°$. The data shown are for two independent runs. The

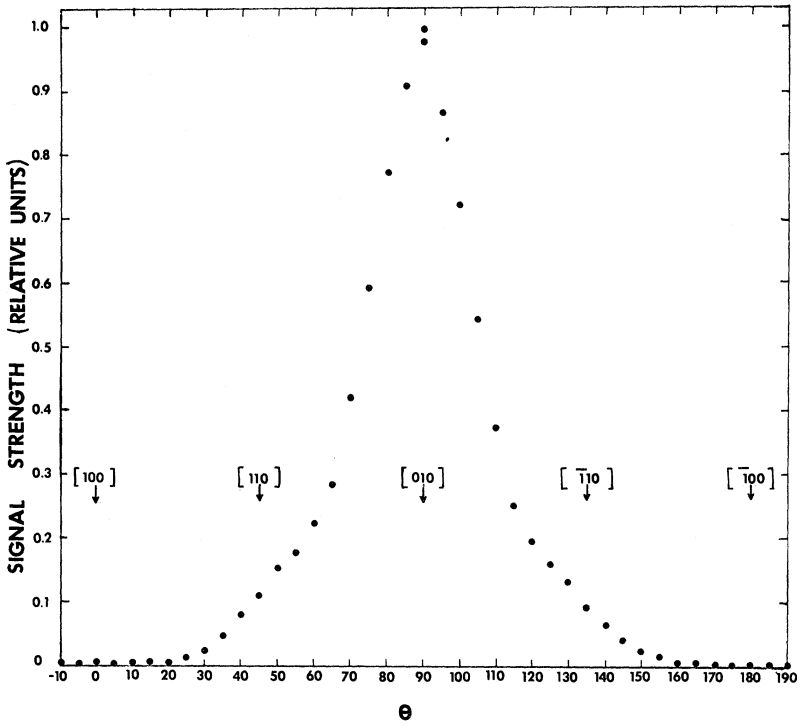

FIG. 2. Angular dependence of the NAR signal strength at 77.4°K. The magnetic field $\vec{H}_0$ is in the (001) plane and θ is the angle between $\vec{H}_0$ and the propagation vector ($\vec{k} \parallel$ [100]) of the acoustic wave. $H_0 = 2940$ Oe, $\nu = 12.155$ MHz.

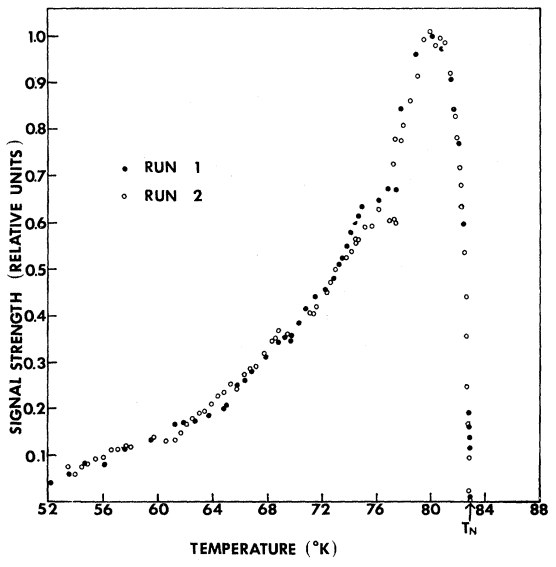

FIG. 3. Temperature dependence of the signal strength for the high-field line with $\theta = 90°$ and a constant peak-to-peak voltage V_T across the transducer of 100 mV. Runs 1 and 2 were made under the same conditions. $\vec{H}_0 \parallel$ [010], $\vec{k} \parallel$ [100], $H_0 = 2940$ Oe, and $\nu = 12.155$ MHz.

most striking feature of the data is the sharp drop in signal intensity near the Néel temperature T_N and the complete absence of any signal above T_N. In contrast, the conventional NMR signal showed no such dramatic change, indicating that the observed spectrum (Fig. 1) was not due to rf leaking around the transducer into the sample. Just below T_N the F^{19} NAR linewidth was 14 ± 0.5 Oe and increased to 30 ± 3 Oe as the temperature was lowered to 70°K. This indicates that the decrease in signal at T_N was due to the vanishing of the coupling mechanism for $T > T_N$ and not to some line-broadening effect as the temperature was increased through T_N. The NMR linewidth showed qualitatively the same behavior, increasing from 12 ± 1 Oe at 83°K to 20 ± 2 Oe at 70°K.

The NAR signal strength peaked at 80°K and then fell off as the temperature was lowered, becoming lost in noise near 50°K. This decrease in signal strength is partially due to the increased saturation which results, presumably, from the longer nuclear spin-lattice relaxation times at lower temperatures. However, the unsaturated signals observed for $T = 77.4$ and 68.5°K were not as large as the signal at 80°K. This

indicates that regardless of saturation, the signal amplitude decreases as the temperature is lowered below 80°K. In order to avoid saturation effects at all temperatures, a technique capable of lower power levels is necessary. This should also enable one to extend the measurements to a lower temperature region.

The behavior of the signal strength as a function of temperature can be reproduced qualitatively if one substitutes the experimental values of the magnetoelastic coupling constant,[7] the anisotropy energy,[8] and the sublattice magnetization (assuming that it follows the Brillouin function for $J=\frac{5}{2}$) into the expression obtained by Silverstein[2] for the strength of the nuclear spin-phonon coupling. Better than qualitative agreement could not be expected due to uncertainties in the experimental data used for the comparison and the limitations of the theory. The temperature dependence of the coupling resulting from the strain-induced modulation of the hyperfine interaction[3] does not appear to follow the data of Fig. 3.

The strength of the observed acoustic resonance may be characterized by the nuclear spin-phonon attenuation coefficient α_n.[1] For the fluorine resonance in $RbMnF_3$ reported here, $\alpha_n \simeq 1\times 10^{-4}$ cm^{-1} at 77.4°K and $\theta = 90°$ as compared with typical values of 10^{-8} cm^{-1} for quadrupolar induced NAR in alkali-halide crystals.[1]

The coupling between the ultrasonic wave and the F^{19} nuclear spin system cannot be due to a nuclear quadrupole or nuclear dipole-dipole interaction. It is not yet possible to determine conclusively from our results whether the two-step process of Silverstein[2] or the direct modulation of the hyperfine interaction at the fluorine nucleus by the ultrasonic strain discussed by Buishvili and Giorgadze[3] is dominant. Both these theoretical calculations were performed for uniaxial systems in low applied fields and at low temperatures; these conditions are not satisfied in the present experiment. Our results do show unambiguously that a very strong resonant coupling exists between the fluorine nuclei and longitudinal coherent ultrasonic waves for temperatures below the Néel temperature in $RbMnF_3$ and that this coupling can be directly observed. It should be possible to utilize this coupling in studying details of the dynamic nuclear spin-lattice relaxation in magnetic materials, as well as determining the temperature behavior of the ratio of the magnetoelastic constant to the anisotropy constant in the important region just below the Néel temperature.

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