0.079, 0.083, and 0.078 Å at 140 K; 0.060, 0.059, and 0.059 Å at 120 K. As $\bar{u}$ is expected to decrease with decreasing temperature, the values for the intermediate phase are substantially larger than those in the phases above and below. In addition, the thermal ellipsoids are highly anisotropic in both low-temperature phases with the major axis along the Ti-Ti bonds. In order to account for the resistivity, susceptibility, and x-ray data in the intermediate phase, it is reasonable to propose that there is charge localization and pairing, but that there is no long-range order in the bonding. The lower transition would then reflect the change from a disordered to an ordered bond state.

In V_4O_7, with one additional d electron per atom, the nature of the transition is markedly different. The variation in intensity with temperature in Fig. 1 shows that the transition is only weakly first order. As there is no change in symmetry at the transition, it cannot be second order. A similar variation with temperature has been observed in the ^{51}V NMR frequency of the 4+ sites,[15] the resistivity,[4] and the susceptibiliy.[6] This suggests that these properties may be related to the pairing of the cations.

There is a strong analogy between the transitions in Ti_4O_7 and V_4O_7 and that envisioned by Verwey for Fe_3O_4. In both cases there is disorder in the cation sites above the transition and charge localization below. However, the crystallographic evidence for a change in cationic size is established only for Ti_4O_7 and V_4O_7. More detailed papers on these structures will be published elsewhere.

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Ultrasonic Studies of Antiferromagnetic Resonance in $RbMnF_3$ near the Néel Temperature

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Peaks found in the attenuation of transverse and longitudinal ultrasonic waves in $RbMnF_3$ below the Néel temperature are identified as due to antiferromagnetic resonance on the basis of their temperature-frequency relation and magnetic field dependence. The temperature dependence of antiferromagnetic resonance has thus been determined for $0.1°K \lesssim T_N - T \lesssim 4°K$, where T_N is the Néel temperature.

The cubic and nearly isotropic antiferromagnet $RbMnF_3$ has been extensively investigated. In particular, various aspects of ultrasonic propagation,[1-7] as well as conventional studies of antiferromagnetic resonance (AFMR),[8,9] have been carried out by a number of workers. As far as

the authors are aware, measurements of AFMR in $RbMnF_3$, in the temperature range $78°K < T < T_N$, in the absence of an external magnetic field, have not been previously reported.

In this Letter, we report results of measurements of the attenuation of transverse and longitudinal ultrasonic waves in the temperature range $78 < T < 85°K$ with special attention given to the region just below the Néel temperature T_N ($T_N \sim 83°K$).

The measurements were carried out on a single crystal of $RbMnF_3$ in the shape of rectangular parallelelepiped $7 \times 5 \times 4$ mm^3, with two pairs of faces normal to $\langle 110 \rangle$ directions and the third pair normal to the [100] direction.[10] The frequency range covered was 90 to 700 MHz for transverse waves and 30 to 510 MHz for longitudinal waves, generated by 30 MHz AC- and X-cut quartz transducers; the pulse-echo method was used.

The waves were propagated in the [001] direction[11] for the longitudinal case, and in the [001] and [110] directions for the transverse case. Some preliminary studies of the effects of magnetic field up to 3 kOe were made with field direction in the $(1\bar{1}0)$ plane.

The temperature of the sample could be stabilized and measured to ±0.005°K. Most experiments were carried out while the temperature changed at a rate of approximately 1°K/h. The temperature was determined to ± 0.02°K.

For $T > T_N$ the ultrasonic attenuation of transverse waves was found to be temperature independent near T_N, in agreement with other observations of the behavior of transverse waves near magnetic phase transitions.[12,13] The attenuation of longitudinal waves exhibited the usual "critical" increase near T_N.[2]

For $T < T_N$ attenuation peaks were observed for both transverse and longitudinal waves. The temperature at which the maximum of the attenuation occurred (T_M) was found to decrease as the ultrasonic frequency was increased. The present results are somewhat similar in appearance to the peaks reported by Moran and Lüthi[3] for longitudinal waves; however, those peaks occur in a much lower temperature region for the same frequencies.

Examples of the observed attenuation peaks (in the absence of an external magnetic field) are shown in Figs. 1 and 2, respectively, for longitudinal waves propagating in the [001] direction and for transverse waves propagating in the [001] direction, with [100] polarization. For the transverse case (Fig. 2), the attenuation behavior at temperatures below the region of the peaks shown was omitted for clarity. The peaks in Fig. 2 are shown from the (temperature-independent) background attenuation level observed, for each frequency, above T_N.

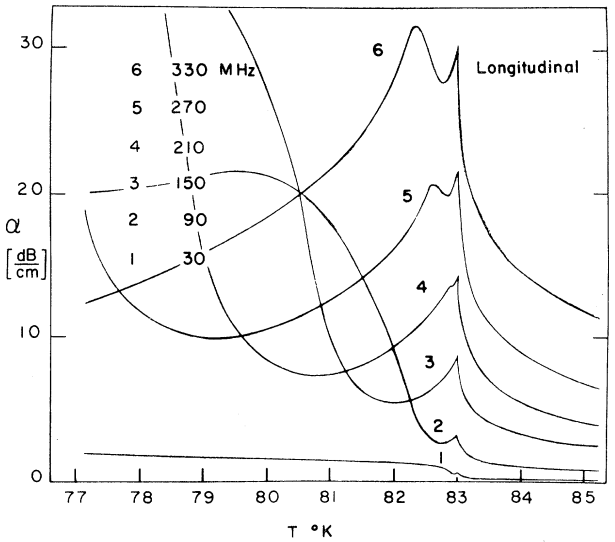

FIG. 1. Peaks in the ultrasonic attenuation (seen on curves 4, 5, 6) for longitudinal waves propagating along the [001] direction in $RbMnF_3$. The "critical" attenuation near the Néel temperature T_N ($T_N \sim 83°K$) is also seen. Frequencies are indicated on the figure (zero external magnetic field).

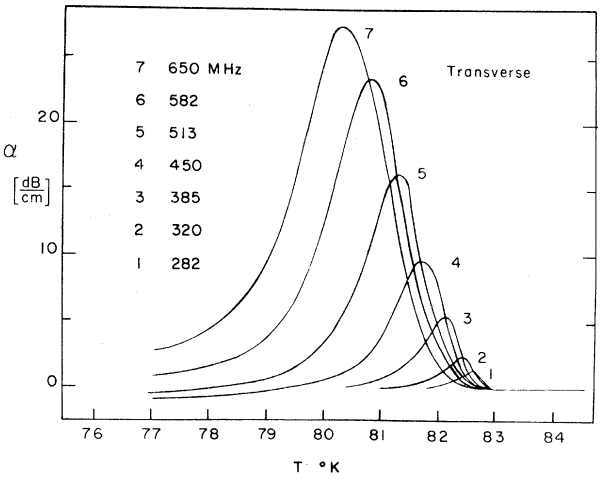

FIG. 2. Peaks in the ultrasonic attenuation of transverse waves propagating along the [001] direction with polarization along the [100] direction in $RbMnF_3$. All the peaks are shown from the background attenuation level measured above the Néel temperature T_N ($T_N \sim 83°K$) for each frequency. Frequencies are indicated on the figure (zero external magnetic field).

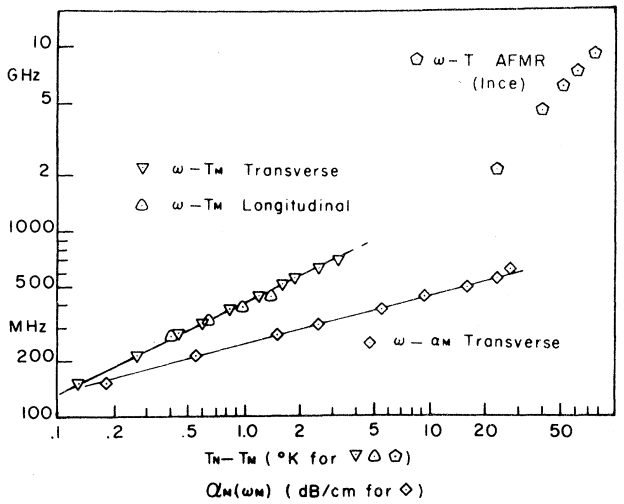

FIG. 3. Relation between the ultrasonic frequency and $T_N - T_M$ (T_M is the temperature at which attenuation maximum occurs for a given frequency), shown by triangles. Relation between ultrasonic frequency and attenuation, α_M, at the maximum for a given frequency, shown by diamonds. The horizontal scale represents both $T_N - T_M$ in degrees, and α_M in dB/cm. Ince's data (Ref. 9) on AFMR are indicated by pentagons. Zero external magnetic field for all cases.

The essential features of the observed peaks are as follows.

(Ia) A plot of the peak frequency ω_M as a function of $T_N - T_M$ is given in Fig. 3. The empirical relation thus found is

$$\omega_M \propto (T_N - T_M)^n , \tag{1}$$

where $n = 0.47 \pm 0.05$ for transverse waves, $n = 0.40 \pm 0.05$ for longitudinal waves, and $T_N - T_M < 4°K$ for the frequency range studied. The transverse-wave peaks were much better defined than the longitudinal ones because of the absence of "critical attenuation."

(IIa) For the transverse waves the attenuation at the peak, α_M, and the frequency ω_M were found to be related by

$$\alpha_M \propto \omega_M{}^{3.8} \propto (T_N - T_M)^{1.8} . \tag{2}$$

(IIIa) Another noteworthy feature, observed without a magnetic field, was that the attenuation peak of the transverse wave of $[1\bar{1}0]$ polarization with propagation direction [110] was much higher than that of [001] polarization with the same propagation direction (~25 and ~4 dB/cm, respectively, for 350 MHz).

(IVa) The application of an external magnetic field $\vec{H}$ has the following effects: (i) for $\vec{H}$ parallel to the direction of propagation of the longitudinal waves (i.e., [001]) the attenuation peak shifts to lower temperatures, the peak height is reduced, and eventually disappears at a field of a few hundred oersteds (for 330 MHz); (ii) for $\vec{H}$ perpendicular to the wave propagation direction ($\vec{H}$ along [110]), no shift is observed in the peak; (iii) for transverse waves, $\vec{H}$ along [001] (i.e., wave propagation direction) causes similar shifts to those observed for the longitudinal waves.

The above experimental results (Ia to IVa) can be accounted for in terms of the resonant coupling of ultrasonic (elastic) waves to the antiferromagnetic spin-wave modes (acoustic AFMR)[5,14,15] through the following features.

(Ib) The temperature dependence of AFMR frequency ω_{AFMR} can be calculated from the relation[16]

$$\omega_{AFMR} \propto (K/\chi)^{1/2} , \tag{3}$$

where K is the anisotropy constant and χ is the perpendicular susceptibility, which can be considered constant for the solution of the form $\omega_{AFMR} \propto (T_N - T)^n$ when $T_N - T$ is small. To evaluate the exponent n, we consider the single-ion anisotropy theory,[17] which accounts successfully for the AFMR observed by Ince[9] at lower temperatures. The temperature dependence of the AFMR frequency (in zero external magnetic field) observed by Ince is shown in Fig. 3. However, near the Néel temperature, this theory predicts $K \propto M^4$, where M is the sublattice magnetization. This prediction can be combined with the results of neutron scattering experiments,[18] which yield $M \propto (T_N - T)^{0.32}$, to give

$$\omega_{AFMR} \propto (T_N - T)^{0.64} . \tag{4}$$

The present experiments yield $n = 0.47$ for the case of transverse waves, suggesting that $K \propto M^3$. (For longitudinal waves $n = 0.40$, but in this case the coupling constant is much larger than for transverse waves and the interactions are more complicated. A detailed treatment of this case will be published separately.) On the other hand, scaling relations yield[18] $M \propto (T_N - T)^{0.285}$; hence

$$\omega_{AFMR} \propto (T_N - T)^{0.57} \tag{5a}$$

in closer agreement with the present experiments.

(IIb) The temperature dependence of α_M can be evaluated as follows. The absorption parameter Γ for transverse sound at resonance with AFMR modes is given by[14]

$$\Gamma = C b_2{}^2/\lambda , \tag{5b}$$

where b_2 is the magnetoelastic coupling constant, λ is the relaxation rate of the AFMR modes, and

C is a substantially temperature-independent parameter with appropriate dimensions. The temperature dependence of b_2 was given by Eastman[8] and can be expressed near the Néel temperature[19] by

$$b_2 \propto M^3 \propto (T_N - T)^{0.96}. \quad (6)$$

The temperature dependence of λ is assumed to be negligible. This is based on the observation that in $RbMnF_3$ the electron paramagnetic resonance linewidth does not show any significant temperature dependence across the Néel point[20,21]; it is further postulated that the temperature dependence of the relaxation rate is the same in the interactions studied here. It thus follows from relations (5) and (6) that

$$\Gamma \propto \alpha_M \propto (T_N - T)^{1.92}, \quad (7)$$

in reasonable agreement with the present result [relation (2)].

(IIIb) Melcher and Bolef[5] calculated ultrasonic-wave interactions with AFM spin-wave modes in $RbMnF_3$ on the assumption that the ultrasonic frequency is much smaller than AFMR and NMR frequencies. It is not unreasonable, however, to assume that the relative values of the coupling constants remain the same for higher frequencies. Their results show that the coupling constants for transverse-wave propagation in [110] are b_1 for $[1\bar{1}0]$ polarization and b_2 for [001] polarization; their experiment, or Eastman's[8] result, gives $b_1 \gg b_2$, indicating that the present result (IIIa) is consistent with theirs.

(IVb) The effect of an applied magnetic field on the observed peaks is also consistent with AFMR. In particular, the observed shift, with magnetic field, in the frequency of the peaks (or of the temperature of the peak at a given frequency), is consistent with a gyromagnetic ratio for electronic spins.

Finally, we examined other effects, such as NMR, antiferromagnetic domains,[22] coupling to an order parameter in the critical region. It was found that none of these could account for the observed features of the ultrasonic attenuation. In conclusion, the observed peaks in ultrasonic attenuation have been identified as due to AFMR, on the basis of their frequency, temperature, and magnetic field dependence.

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