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Ultrasonic Attenuation near the Critical Point of MnF_2

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Ultrasonic attenuation and velocity have been measured in MnF_2 in the vicinity of the Néel temperature. Longitudinal and transverse waves were propagated in the [110] and [001] directions. Peaks in the attenuation for longitudinal waves were observed for both directions of propagation. Both peaks occur at the Néel temperature and no velocity change at this temperature was observed for any mode of propagation. The data are in qualitative agreement with recent calculations.

INTRODUCTION

THE compound MnF_2 is a well-known antiferromagnet with a Néel temperature of 67.336°K as determined by NMR.[1] Its structure is tetragonal rutile with a room temperature c/a ratio of 0.675. In the region of the Néel temperature, the c/a ratio changes[2] because of a small contraction in the direction of spin alignment but there is no associated structural change.

Several years ago one of us published some preliminary measurements on ultrasonic attenuation in MnF_2.[3] These data, for propagation in the [110] direction, showed a peak in longitudinal wave attenuation near the Néel temperature. The peak height increased with frequency and was unaffected in size and position by the magnetic fields available. No attenuation peak was observed for shear waves and no velocity change was observed for either longitudinal or shear waves. These results differed from those obtained in experiments with other antiferromagnetic materials. Chromium[4,5] showed a dip in Young's modulus at the Néel temperature and an increase in internal friction starting at the Néel temperature and reaching a maximum at the "spin-flip" temperature. Other experiments on the oxides of cobalt,[6] nickel,[7] and manganese[8] showed similar effects: A lowering of modulus and an increase in internal friction as the temperature is decreased through the critical temperature.

Since publication of the first results on MnF_2, the ferromagnetic transition in gadolinium[9,10] and the antiferromagnetic transition in MnTe,[11] UO_2,[12] and $RbMnF_3$ [13,14] have been investigated ultrasonically. In all of these latter experiments either the ultrasonic attenuation or velocity, or both, showed anomalies in the region of the critical temperature, and several theoretical calculations[15–18] have been advanced to explain the results. The mechanism is thought to be one in which the sound wave produces oscillations of the distance between neighboring spins and thus oscillations in the exchange interaction between them. This interaction between sound waves and spins gives rise to an attenuation of the sound wave which increases near the critical temperature where the thermal spin fluctuations become large, and there are regions where the correlation distance extends over large numbers of spins. The calculations are complex and approximate in the treatment of spin correlations so that the results depend to some extent on the approximations.

The experimental work described in this paper is an extension of the early work and is in qualitative agreement with the theory of Pytte and Bennett.[18] The results suggest a mechanism of volume magnetostriction and indicate that the behavior of the spin diffusion coefficient in the transition region needs to be better understood.

EXPERIMENTAL

The experiments described here are measurements of ultrasonic velocity and attenuation of both longitudinal and shear waves propagating in two directions in MnF_2. Short rf pulses supplied by an Arenberg or Matec pulsed oscillator were applied to a transducer-sample configuration, receiver, and time-base generator in the usual

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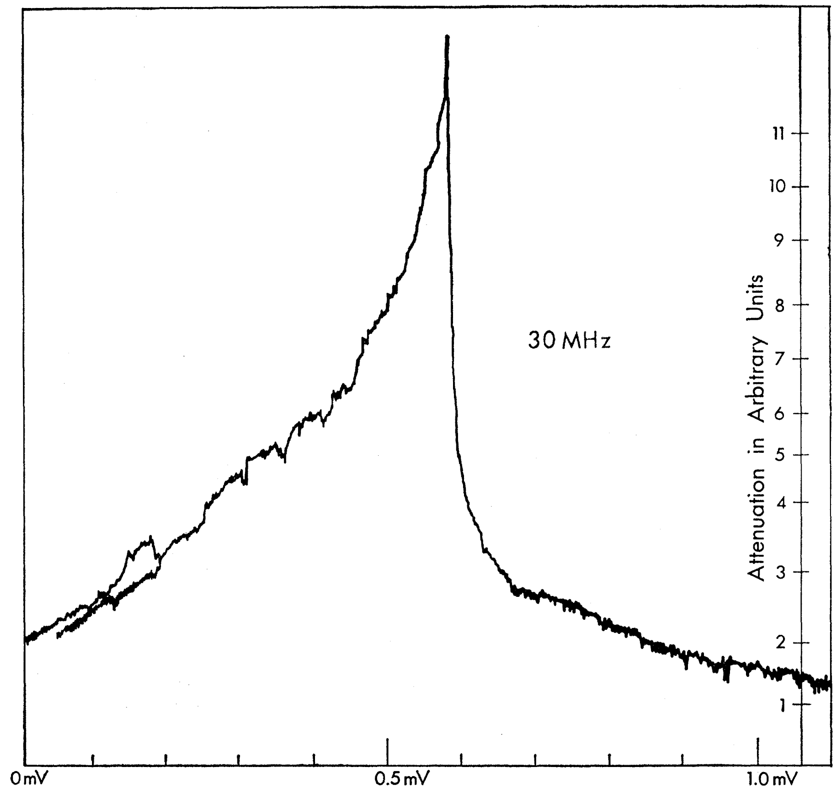

FIG. 1. x-y record of attenuation versus thermometer output voltage. The total temperature interval covered is approximately 6°C.

pulse-echo fashion.[19] The sample was immersed in a temperature bath of either pumped liquid nitrogen or oxygen, whose pressure was controlled by a manostat. Temperature was measured with a platinum-wire resistance thermometer placed in contact with the specimen. For most of the measurements two different crystals of MnF_2 were used. One crystal had faces cut so that ultrasonic propagation was parallel to [110][20]; in the second crystal, propagation was parallel to [001].[21] As prepared for use, the crystal lengths were 1.386 cm for the [110] and 1.285 cm for the [001]. The [001] sample was later polished to develop [110] faces and a number of measurements were made on this specimen to confirm that the differences in attenuation were due to anisotropy and not the method of manufacture. Several other crystals were used in attempts to measure in the [100] direction. Polishing difficulties and the extremely high attenuation along this axis precluded any quantitative results.

Changes in wave velocity were determined by observing the transit time of an echo which had undergone multiple reflections. A change in transit time of 0.01 μsec could be detected out of a total transit time of about 50 μsec, making a relative precision of slightly better than two parts in 10^4. At the critical point, no discontinuous change in ultrasonic transit time was observed for longitudinal or shear waves propagating in either crystal.

An associated change in modulus will be the sum of the changes in transit time and the changes in length due to thermal expansion. Using the measured values of thermal expansion[22] and choosing a conservative 2°C temperature interval, the thermal effect is small compared to the upper limit of our ability to measure changes in transit time. Thus, in the critical region the change in modulus is less than four parts in 10^4.

The attenuation measurements were taken with an automatic attenuation comparator[23] which measures the height of a particular echo and whose output is a dc voltage proportional to the logarithm of the echo height. This output was displayed on the vertical channel of an x-y recorder, and an amplified voltage from the platinum resistance thermometer was fed into the horizontal channel. The attenuation scale was calibrated by insertion of precision attenuators. The platinum resistance thermometer was calibrated by comparison with a second platinum resistance thermometer which had been previously calibrated by the National Bureau of Standards. Using the automatic recording techniques, curves of attenuation versus temperature were traced

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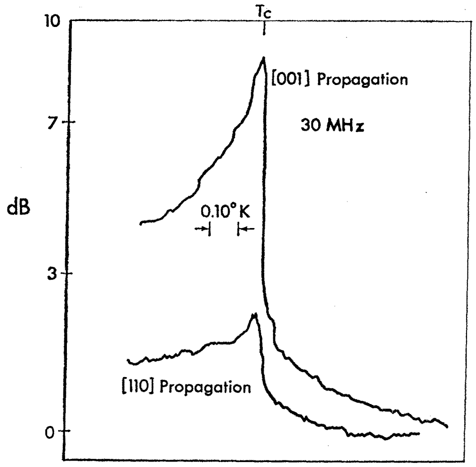

FIG. 2. Portion of an x-y record of attenuation versus temperature for 30-MHz longitudinal wave propagation in the [110] and [001] directions.

out for longitudinal and shear waves propagating in the [001] and [110] directions for frequencies between 10 and 70 MHz. No attenuation peak was observed near the Néel temperature for shear waves propagating in either direction at frequencies up to 190 MHz. This is in agreement with the earlier results[3] and was later reconfirmed by visual observations of an echo pattern at 300 MHz. In this latter case, a thin-film CdS transducer was used with which both longitudinal and transverse modes were excited. In the critical region the longitudinal echoes disappeared while the shear mode was unaffected.

In the critical region, peaks in the longitudinal wave attenuation were observed for both directions of propagation. Figure 1 shows one of the x-y records for [001] propagation of 30-MHz longitudinal waves. Here the λ-like character of the attenuation peak is clearly discernible, and the data presented represent a considerable improvement over the preliminary results.[3] The slight nonlinearity of the vertical scale arises in the i.f. amplifier of the detector. The horizontal scale is calibrated in millivolts and the resistance-temperature curve must be used to convert to temperature. For the voltage range shown here, the corresponding temperature range is approximately 6°. The pump pressure was changed slowly enough so that the time to trace the entire curve was over 1 h. Some of the noise shown in the figure is attributable to bubbling of the liquid nitrogen in which the crystal was immersed. Curves similar to Fig. 1 were traced out for frequencies varying from 20 to 70 MHz for both directions of propagation.

In order to determine whether the attenuation peaks occurred at different temperatures for the two directions of propagation, an experiment was performed in which both crystals were mounted adjacently in the cryostat and both in contact with the resistance thermometer. A curve for one crystal was traced; then the bath was warmed to a temperature above the Néel point and a curve for the other crystal was obtained. The only change was to reconnect the rf pulser from one specimen to the other so that any possible thermal hysteresis effects occurring in the thermometer when it is warmed to room temperature were eliminated. The results of this experiment are shown in Fig. 2, which is a portion of a record made using an expanded horizontal scale. Both records are for 30-MHz longitudinal waves. Over this narrow temperature interval, the resistance temperature characteristic of the thermometer is essentially linear and the horizontal distance corresponding to a small temperature interval (0.10°K) is marked on the figure. The time to record the portion of the traces shown is slightly less than 30 min in each case.

Several features characteristic of all the experiments are shown in Fig. 2. All the peaks are λ-like and always, for a given frequency, the ultrasonic attenuation in the vicinity of the Néel temperature and especially in the vicinity of the peaks is greater for propagation in the [001] direction. In the figure, a total attenuation of 10 dB corresponds to an attenuation coefficient of approximatly 3.9 dB cm^{-1}. Another common feature is that below the transition temperature the attenuation decreases more rapidly for [001] propagation. Finally, it is evident that both peaks in the attenuation do occur at the same transition temperature. Experimentally, the transition temperature T_c is the Néel temperature to within experimental error.

Figure 3 is a log-log plot of attenuation versus $(T-T_c)$ for 30-MHz longitudinal waves propagating in the [001] direction. The points were obtained from curves similar to Fig. 1. The correct temperature and attenuation were then determined for each point from the calibrations. In addition, the attenuations were corrected by a small amount which is our estimate of the residual attenuation in the sample due to other causes. In all cases this correction was less than 0.35 dB cm^{-1}. Plots for the other direction and other frequencies are

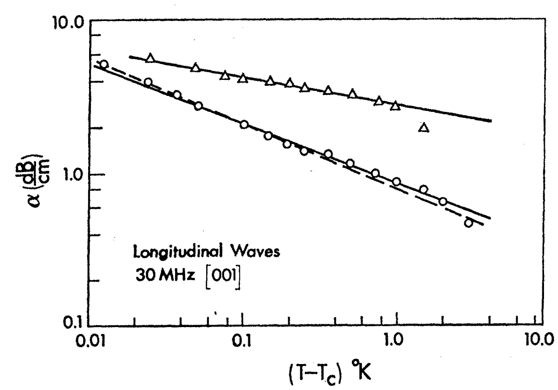

FIG. 3. Log-log plot of attenuation coefficient versus temperature difference as measured from the critical temperature. The figure is for 30-MHz longitudinal wave propagation in the [001] direction and was constructed from x-y curves similar to Fig. 1.

similar, but this figure represents the best data. The triangles mark points taken for temperatures below T_c; the circles mark points taken above the transition temperature. It is evident that a power-law relation holds for both sets of points, which cover approximately two orders of magnitude in $(T-T_c)$. For the points marked with triangles, the line drawn through the points give the exponent of $(T-T_c)$ to be -0.18. For the points marked with a circle, the best line through all the points gives an exponent of -0.42. If one chooses to ignore the higher-temperature points, then the dashed line through the points for which $(T-T_c)\leq 0.25$ gives an exponent of -0.39.

The last few points which correspond to relatively large values of $(T-T_c)$ tend to depart from straight-line behavior. This feature is a characteristic of all of our plots. The position of these attenuation points is more sensitive to the estimated correction since the estimate is a larger fraction of the total attenuation. In contrast, the slopes of the lines in Fig. 3 are relatively insensitive to the correction estimate. Making no correction in Fig. 3 yields exponents of -0.26 and -0.50.

For [110] propagation at 30 MHz analysis of a plot similar to Fig. 3 gives an exponent of -0.38 for temperature above T_c. For obscure reasons the low-temperature data are always so scattered as a result of fluctuations in the original trace that a meaningful exponent cannot be obtained. At frequencies higher than 30 MHz, both the over-all attenuation and the peak attenuation increase so that measurements become increasingly less precise. Analysis of the $T>T_c$ data up to 70 MHz leads to exponents between -0.40 and -0.50 for [001] propagation. At 90 MHz and above, the echoes are generally small and as the attenuation peak is approached, the signal amplitude drops enough to be unmeasurable. The best results are at 30 MHz for both propagation directions.

From 10 to 70 MHz the measurements are thought to be reliable enough to give a rough estimate of the frequency dependence of the attenuation peak. For both directions this dependence is approximately that the peak height is proportional to ω^2. Visual observations have been made at frequencies up to 440 MHz using cadmium sulfide transducers. At these higher frequencies, all the effects described still persist: A large velocity change was not apparent, the attenuation peak still is apparent and is large, and no large attenuation peak is evident for shear waves.

DISCUSSION

The results of these experiments on ultrasonic propagation in single-crystal MnF_2 in the region of the Néel temperature are as follows:

(a) Near the Néel temperature a λ-like peak is observed in the attenuation of longitudinal waves.

(b) The attenuation for longitudinal waves propagating parallel to [001] is always greater than the attenuation for propagation parallel to [110].

(c) Both peaks occur at the same temperature, which is very close to the Néel temperature.

(d) In the range of frequencies used (10–70 MHz) there is no change in transition temperature with frequency and the peak attenuation for both directions of propagation is roughly proportional to the square of frequency.

(e) No attenuation peak is observed near the Néel temperature for shear waves propagating parallel to the [001] or [110] directions.

(f) No large modulus change is observed for shear or longitudinal waves for propagation parallel to either the [001] or [110] directions.

These results are similar to the results of other recent ultrasonic measurements. In $RbMnF_3$, MnTe, and Gd a peak in the longitudinal wave attenuation is observed at the ordering temperature and the size of this peak is proportional to ω^2. If the attenuation is assumed to follow a temperature dependence of the form $(T-T_c)^{-\eta}$ near the Néel temperature, the resulting η values are 0.32 and 1.20 for $RbMnF_3$ and Gd. Thus the MnF_2 η values of 0.42 and 0.38 for the two different directions of propagation are comparable with the η values for the other antiferromagnet and substantially less than that observed for the ferromagnet as predicted by the theory of Pytte and Bennett.[18]

In Gd the attenuation also showed anisotropy. No shear-wave attenuation peaks are found in Gd, and this fact is interpreted as indicating that the spin-phonon coupling is of the volume magnetostrictive type. In addition, the temperature dependence of attenuation for $T<T_c$ is found to be much weaker.

The principal difference between the measurements on MnF_2 and measurements on the other materials is the lack of a velocity change in MnF_2 at the transition temperature. Relatively large velocity changes are found for both $RbMnF_3$ and Gd, while the change for MnTe is quite small (3×10^{-3}) but still observable.

The phenomenological calculations of Belov[8] and Papoular[24] predict a shift in the peak of the attenuation with frequency. This prediction is contrary to the present results and those for $RbMnF_3$ and MnTe, although in the latter material a second peak below the Néel temperature is observed to shift with frequency. The various theories are attempts to incorporate the spin-phonon interaction and to calculate the influence of thermal fluctuations via multispin correlations. The calculations are complex and of necessity approximate. Unfortunately, the results are dependent on the method of approximation. However, all predict that the ultrasonic attenuation α is given by

$$\alpha\sim\omega^n(T-T_c)^{-\eta}. \quad (1)$$

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Papoular predicts $n=1$ and $\eta=\frac{3}{2}$, Tani and Mori predict $n=2$ and η lying between $\frac{1}{2}$ and 1. Bennett and Pytte also predict $n=2$ and an η value between 1 and 2, depending on the behavior of the spin diffusion coefficient.

Additionally, the Bennett-Pytte calculations show that for ultrasonic attenuation the antiferromagnetic transition is less singular than the ferromagnetic; the ultrasonic attenuation is more singular than the specific heat[25]; and the attenuation in a ferromagnet is greater than in an antiferromagnet. All of these predictions are in agreement with the results of these and other experiments.

On the other hand, the calculations of Tani *et al.*[16] do predict the correct anisotropy of peak attenuation. The Bennett-Pytte theory seems to have more correct predictions and to be in better agreement with the results of this work. In view of (e) above it appears that the Bennett-Pytte calculation using spin-phonon coupling of the volume magnetostriction type best fits the experimental results of MnF_2.

It is of interest to compare the results of the Bennett-Pytte calculation with the present experimental results. Their calculation yields a temperature-dependent attenuation coefficient

$$\alpha \sim \chi'^{1/2}/\Lambda, \tag{2}$$

where Λ is the spin diffusion coefficient and χ' is the wave-vector–dependent susceptibility. Present theories indicate that

$$\chi' \sim (T-T_c)^{-\gamma}, \tag{3}$$

where γ is the same for both ferromagnets and antiferromagnets and has a value between 1 and 2 depending on the method of calculation.

The behavior of Λ near T_c is not well understood. It is believed that

$$\Lambda \sim (\chi')^{-r}, \tag{4}$$

where r has been calculated to be $\frac{1}{4}$ (Ref. 26) or 1.[27] Using these values of Λ and χ', the attenuation coefficient is then

$$\alpha \sim (T-T_c)^{-\gamma[(1/2)+r]}. \tag{5}$$

The experimental value of the exponent of $(T-T_c)$ is -0.42. Any combination of the above estimates of r and γ leads to an exponent substantially larger in magnitude than the experimental value.

In addition to ultrasonic attenuation, the specific heat for an antiferromagnet has been estimated by Bennett and Pytte to vary as $C \sim (T-T_c)^{-\gamma/2}$. The specific-heat data[25] seem to show a logarithmic singularity but can be fitted with an inverse power law with an exponent value less than 0.1. The values of γ mentioned above predict a much stronger temperature variation of the specific heat. The difference between theoretical prediction and experiment for both the ultrasonic attenuation and the specific heat point out that a better understanding of the spin-diffusion coefficient is needed and that the approximations in the theory do not properly take into account anistropy and also possibly tend to overestimate the critical fluctuations.

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