Ultrasonic Attenuation near the Soft-Mode Transition in $KMnF_3$[†]

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The frequency and temperature dependence of the longitudinal ultrasonic attenuation along the [123] direction of $KMnF_3$ has been measured above the structural phase transition near $T_A = 186$ K. The attenuation of 30, 90, and 270-MHz sound was measured and was found to have a critical contribution which diverges as $\Delta\alpha = A\,\omega^x \epsilon^{-\eta}$ (with $x = 1.18 \pm 0.03$ and $\eta = 1.30 \pm 0.04$) in the region $0.001 < \epsilon < 0.10$, where $\epsilon = (T - T_A)/T_A$. Additional data taken at 150 MHz support this conclusion. The best fits over the whole range of ϵ were found by allowing the background attenuation to be a varying parameter of the fit. We do not observe any evidence of the crossover behavior predicted by Schwabl and reported by Fossheim *et al.*, nor do we see the ω^2 dependence predicted by Pytte and by Schwabl.

$KMnF_3$ is one of a group of perovskite crystals in which softening of a phonon mode results in a structural transition from the cubic perovskite to a tetragonal phase.[1,2] Neutron diffraction measurements by Gesi, Axe, Shirane, and Linz[3] have shown that the Γ_{25} phonon mode at the R point of the Brillouin zone goes soft at 185 K. Specific heat measurements by Furukawa, Fujimori, and Hirakawa[4] have shown that the transition is of first order and occurs near the expected second-order phase change.

Several theories of ultrasonic attenuation near soft-mode phase transitions have been proposed. In particular, for $KMnF_3$ the R-point soft mode decreases rapidly in energy as the temperature decreases towards T_A, and through mode-mode coupling it affects the behavior of the acoustic zone-center modes in a dramatic manner. Pytte[5] predicts that $\Delta\alpha$ (the critical part of the attenuation) should obey $\Delta\alpha \sim \omega^2\epsilon^{-3/2}$ if $\Gamma \gg \omega$ and $\Delta\alpha \sim \omega^2\epsilon^{-1/2}$ if $\Gamma \ll \omega$, where Γ relates to the damping of the soft mode and $\epsilon = (T - T_A)/T_A$. The former criterion is valid for our measurements on $KMnF_3$ where the mode has been observed to be highly overdamped.[3] Earlier Tani and Tsuda[6] had predicted $\Delta\alpha \sim \omega\epsilon^{-3/2}$, however, Pytte[5] suggests that their theory may be an oversimplification.

Recently Schwabl[7] predicted $\Delta\alpha \sim \omega^2\epsilon^{-1.25}$ very close to T_A, crossing over to $\Delta\alpha \sim \omega^2\epsilon^{-\eta}$ far from T_A (where $\eta = \gamma_d - d\nu_d + 2$). Ising values give $\eta = 1.75$ for a dimensionality of 2. The dimensionality could well be important due to the extremely flat dispersion of the soft-mode branch from the R point to the M point in the Brillouin zone. In addition, Schwabl has taken account of the central mode[8] observed in $KMnF_3$ which is now known[9] to accompany the soft-mode response.

The theories of Pytte[5] and Schwabl[7] predict a quadratic frequency dependence while Tani and Tsuda[6] predict that $\Delta\alpha$ will be linear in ω. The predicted ϵ exponents vary from 1.25 to 1.75 and Schwabl predicts a crossover behavior. The purpose of the present experiment is to obtain data over wide enough frequency and temperature intervals to test these theories.

Courdille and Dumas[10] have reported that the longitudinal ultrasonic attenuation measured at 680 MHz diverges as $\epsilon^{-1.4}$ along the [100] direction and as $\epsilon^{-1.25}$ along [111]. Furukawa *et al.*[4] report that the longitudinal attenuation along [100] behaves as $\omega\epsilon^{-1.3}$. Their measurements were made at 20 and 60 MHz and were taken over the range $0.0025 < \epsilon < 0.018$. Although their analysis seems to indicate a temperature exponent η of 1.3 and a relatively weak frequency dependence $x \sim 1$ (actually $\Delta\alpha \sim \omega^{1.25}$ fits their data), it was felt that data over a wider range of ϵ and ω were necessary to determine these exponents with more confidence. In particular, it is often possible to accommodate a large range of temperature exponents if one is fitting over less than one decade in ϵ and if T_A and background are adjustable parameters in the analysis. This problem is compounded when one is trying to determine the two exponents and x and η simultaneously.

The ultrasonic-attenuation measurements were made using the pulse-echo technique. An X-cut quartz transducer served as generator and receiver of 30-, 90-, and 270-MHz longitudinal sound along the [123] axis ($\pm 1°$) of a single crystal of $KMnF_3$. The faces of the crystal were 1.00 cm apart and less than 6×10^{-4} rad out of parallel. The total attenuation per echo could be determined to a precision of ± 0.02 dB for $\alpha < 10$ dB per echo and to within 2% for $\alpha > 10$ dB per echo. A slow temperature-drift technique was used which allowed

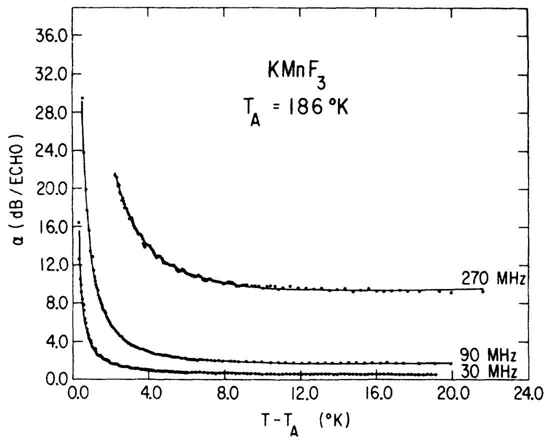

FIG. 1. Longitudinal ultrasonic attenuation along the [123] direction in $KMnF_3$ vs $T - T_A$.

drifts slower than 3 K/h. Even slower drifts produced no measurable change in the $\alpha(T)$ data. A Cryogenic Linear Thermometer was used to monitor the temperature. Although the sensitivity of these thermometers allows T to be determined to a precision of ± 0.01 K the absolute accuracy and repeatability is on the order of ± 0.5 K.

Figure 1 shows the total attenuation in dB per echo for 30, 90, and 270 MHz from $\epsilon = 0.001$ to $\epsilon = 0.01$. The total attenuation α is the sum of the critical part $\Delta\alpha$ and a background term α_B. The background term contains contributions from the attenuation at the bond as well as noncritical attenuation in the sample itself. After repeated temperature cyclings the total attenuation returned to the same value indicating that the bond attenuation was not changing.

In order to test the theories mentioned above the data for all frequencies were fit to one nonlinear-least-squares solution to obtain all parameters. The form was

$$\alpha(\omega, T) = A\omega^x \epsilon^{-\eta} + B_\omega + C_\omega T, \qquad (1)$$

where the first term represents the critical part of the attenuation, the second and third terms are the background. The background and T_A were allowed to vary for each of the frequencies, the latter variation being due to the lack of absolute reproducibility of the thermometer.

TABLE I. Best-fit values for the parameters T_A, B_ω, and C_ω at 30, 90, and 270 MHz. These parameters occur in the expression for the ultrasonic attenuation $\alpha = A\omega^x\epsilon^{-\eta} + B_\omega + C_\omega T$, where $\epsilon = (T - T_A)/T_A$. The best fit values for A, x, and η are $6.31 \times 10^{-5} \pm 1.75 \times 10^{-5}$ dB echo^{-1} MHz$^{-1.18}$, 1.18 ± 0.03, and 1.30 ± 0.04, respectively.

ω (MHz)	T_A (K)	B_ω (dB echo^{-1})	C_ω (dB echo^{-1} K^{-1})
30	185.72 ± 0.01	0.400 ± 0.012	$(5.07 \pm 37.0) \times 10^{-3}$
90	185.15 ± 0.02	-4.69 ± 1.08	$(3.05 \pm 0.05) \times 10^{-2}$
270	185.91 ± 0.05	-13.59 ± 1.72	$(1.08 \pm 0.08) \times 10^{-1}$

The results of the analysis are shown in Table I. It is seen that the best values for x and η are 1.18 ± 0.03 and 1.30 ± 0.04 respectively. For each of the three frequencies there were 166 data points in the temperature range 185–205 K. The curves through the data of Fig. 1 are those calculated from the results in Table I. Figure 2 shows the critical part of the attenuation $\Delta\alpha$ versus ϵ on a log-log plot with the best fits shown.

The values shown in Table I have utilized all of the data taken over the range 185–205 K. Data over restricted temperature intervals of 185–200 K and 185–190 K and 185–188 K were also fit to Eq. (1). The resulting values of the parameters, x and η showed no variation greater than the listed errors.

In addition to the fits mentioned above the data were also analyzed with parameters C_ω fixed to those determined by the slope of the high-temperature attenuation (measured in the range 250–300 K where the critical attenuation should be negligible). The latter C_ω were determined by separate experimental runs. The resulting fits were much poorer with an apparent systematic deviation from the data over much of the region 195–205 K for the 30- and 270-MHz cases. This indicates that either the slope of the background is not constant over the extended range 185–300 K or that a variation had occurred in the two separate runs to determine C_ω. In addition, the results for the temperature exponent η depended on the range of ϵ utilized in the fit when the C_ω were fixed at the high-temperature values.

Plots of the weighted variance versus the parameter x (the frequency exponent) clearly demonstrat-

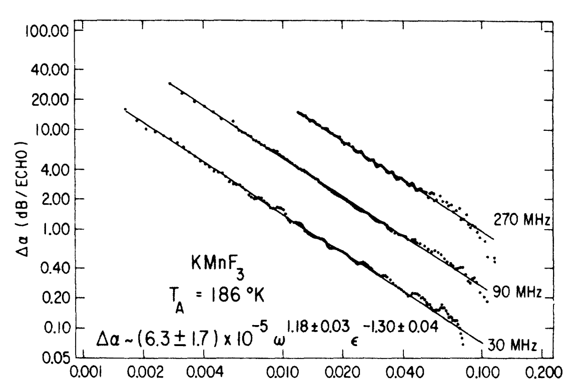

FIG. 2. Critical part of the longitudinal ultrasonic attenuation vs $\epsilon = (T - T_A)/T_A$ for the [123] direction in $KMnF_3$.

ed that the value of 1.18 is insensitive to the choice of background and range of data fit. Finally, a separate run was made at 150 MHz for $0.008 < \epsilon < 0.17$ giving $\eta = 1.21 \pm 0.06$.

At the conclusion of this work we became aware of work to be reported by Fossheim *et al.*[11] in which they observe a crossover between two different exponents as predicted by Schwabl.[7] Fossheim *et al.*[11] have measured the longitudinal attenuation in the [100] direction at 10 MHz for a range $0.0008 < \epsilon < 0.05$ and report that the critical part of the attenuation shows a crossover behavior at $\epsilon \simeq 0.005$. In particular, they report $\Delta\alpha \sim \epsilon^{1.25}$ for $0.0008 < \epsilon < 0.005$ and $\Delta\alpha \sim \epsilon^{-1.95}$ for $0.005 < \epsilon < 0.015$. A frequency dependence of $\omega^{-1.4}$ was also determined.

This crossover has not been observed by us in the [123] direction for measurements at four different frequencies over the range $0.001 < \epsilon < 0.1$. Moreover, we obtain $\Delta\alpha \sim \epsilon^{-1.3}$ over the entire temperature range in agreement with the behavior observed by Furukawa *et al.*[4] and by Fossheim *et al.*[11] near to T_A.

It is apparent that the analysis of the present data indicates that a good fit has been obtained over the whole range of ϵ by allowing the background to be a fitted parameter. The data of Fossheim *et al.*[11] show an extremely small remanent background attenuation at 10 MHz which apparently causes no ambiguity in their analysis. To further explore the possibility of the crossover region in the present data, we have taken all points with $\epsilon > 0.01$ and calculated the weighted variance for fits with the various values $1.3 < \eta < 2.0$. In this analysis the T_A were held fixed at the values found from fitting all the data. The weighted variance had a minimum of 0.010 at $\eta = 1.4$ increasing to 0.027 at $\eta = 2.0$, the latter fit being statistically untenable for $\simeq 400$ data points. Here the slight increase observed in η could be due to the inclusion of data at large T which are not in the critical region.

Finally, it is clear from all reported measurements that $\Delta\alpha$ is not proportional to ω^2. As mentioned above, our determination of $\Delta\alpha \sim \omega^{1.18}$ is insensitive to background and range of data fit. It is apparent that the theories of Pytte[5] and Schwabl[7] which predict $\Delta\alpha \sim \omega^2$ have some shortcoming in this respect and that some unknown aspect of the $KMnF_3$ soft-mode phase transition is in evidence.

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[1] W. Cochran and A. Zia, Phys. Status Solidi **25**, 273 (1968).
[2] H. Thomas and K. A. Muller, Phys. Rev. Lett. **21**, 1256 (1968).
[3] K. Gesi, J. D. Axe, G. Shirane, and A. Linz, Phys. Rev. B **5**, 1933 (1972).
[4] M. Furukawa, Y. Fujimori, and K. Hirakawa, J. Phys. Soc. Jap. **29**, 1528 (1970).
[5] E. Pytte, Phys. Rev. B **1**, 924 (1970).
[6] K. Tani and N. Tsuda, J. Phys. Soc. Jap. **26**, 13 (1969).
[7] F. Schwabl, Phys. Rev. B **7**, 2038 (1973).
[8] K. Tani, J. Phys. Soc. Jap. **26**, 93 (1969).
[9] S. M. Shapiro, J. D. Axe, and G. Shirane, Phys. Rev. B **6**, 4332 (1972).
[10] J. M. Courdille and J. Dumas, Solid State Commun. **9**, 609 (1971).
[11] K. Fossheim, D. Martinsen, and A. Naeso (unpublished); K. Fossheim, D. Martinsen, and A. Linz, in Proceedings of the NATO A.S.I. Meeting, 1973 (unpublished).