Velocity of Sound in MnF_2 near the Néel Temperature*

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The anomalous change of the velocity of sound near the Néel point was measured in MnF_2 for the longitudinal waves propagating along the [110], [100], and [001] directions. The measured result did not show any dispersion. The anomaly as a function of temperature was described by the power-law formula, $\Delta V/V_0 \sim |T-T_N|^{-\zeta}$, with the critical exponent ζ equal to 0.12 for $T>T_N$, and 0.02 for $T<T_N$, for all these longitudinal waves. A significant anisotropy was found, however, in the magnitude of the anomalous change. These results were well explained by a theoretical treatment, by which a relative value of the derivatives of the dominant exchange interaction J_2 was deduced to be $|(\partial J_2/\partial z)/(\partial J_2/\partial x)|=2.7_7$, a value in good agreement with other experimental results. Finally, combining present sound-velocity data with those on attenuation, the existence of a relaxation time of 3×10^{-9} sec is suggested over the temperature range of $T-T_N \gtrsim 2\times10^{-2}$ °K in the paramagnetic phase, and implications of this relaxation time are discussed.

I. INTRODUCTION

SOUND velocity as a function of temperature has a sharp dip at the critical point of the second-order phase transition.[1–5] This anomalous variation of the velocity can usually be described by a power-law formula,

$$-\Delta V/V_0 \sim \omega^n |T-T_N|^{-\zeta}, \tag{1.1}$$

where ΔV is the anomalous change of the velocity from a normal variation which would be expected if there were no phase transition, V_0 is the velocity of the normal variation at the critical point T_N, ω is the angular frequency of sound, and n and ζ are the quantities to be compared with theory.

The study of the sound velocity near the phase-transition point is as important as that of the sound attenuation because the sound velocity in the low-frequency limit does not involve the relaxation times of the problem, and its anomaly near the transition point can therefore be treated by considering only the static part of the fluctuation. This situation makes the problem much simpler than that of the attenuation of sound. The magnitude of the anomalous change in the sound velocity gives us a useful information of the strength of the coupling between spins in the system and acoustic phonons. Furthermore, if we combine the sound velocity and the sound attenuation measurements, we may determine the characteristic relaxation time, which should also be an important quantity in the problem with which we are concerned.

A number of experiments have been carried out to study acoustic properties of MnF_2 near the Néel point.[6–8] One of us (A.I.) has roughly determined the relative value of the derivatives of the exchange interactions from the attenuation measurement.[9] The anomaly of the sound velocity has also been investigated preliminarily in this material,[3] which revealed a peculiar fact that the critical exponent ζ in the above formula Eq. (1.1) for the [100] longitudinal waves was very close to the critical exponent for the attenuation coefficient, implying that the relaxation time now would depend very weakly on the temperature.[10]

In this paper, we report a similar, more detailed investigation in MnF_2, varying the frequency and the propagation direction of the sound to look for a possible dispersion of the velocity and the anisotropy in both the critical exponent and the magnitude of the velocity change.

In Sec. II, the experimental procedure of the measurement is reported. The result of the experiment is presented in Sec. III. A theory of sound-velocity changes is given in Sec. IV. Finally, the discussion of the experimental result on the basis of this theory is presented in Sec. V.

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[1] R. L. Melcher, D. I. Bolef, and R. W. H. Stevenson, Solid State Commun. 5, 735 (1967).

[2] B. Golding, Phys. Rev. Letters 20, 5 (1968).

[3] A. Ikushima, Phys. Letters 29A, 364 (1969).

[4] T. J. Moran and B. Lüthi, report prior to publication and private communication.

[5] B. Lüthi and R. J. Pollina, Phys. Rev. Letters 22, 717 (1969).

[6] J. R. Neighbours and R. W. Moss, Phys. Rev. 173, 542 (1968).

[7] R. G. Evans, Phys. Letters 27A, 451 (1968).

[8] A. Ikushima, J. Phys. Chem. Solids 31, 283 (1970).

[9] A. Ikushima, J. Phys. Chem. Solids (to be published).

[10] In the experiment quoted, the attenuation of sound grows with frequency ω as $\omega^{1.7}$. Therefore, the relaxation time deduced, and its temperature dependence especially, must be regarded as only qualitative.

II. EXPERIMENTAL PROCEDURE

A system for the present measurement is in principle the same as that reported by McSkimin,[11,12] but modified extensively by Holder.[13] We will briefly describe the system here.

Figure 1 is a block diagram of the system. Two frequency synthesizers[14] were used; one of these maintained the repetition frequency of pulses at a multiple of the round-trip transit time of the pulses in the specimen, and the other gave the oscillation of the carrier frequency. The pulses were generated by a gated amplifier[15] and fed through a matching network[16] to a quartz transducer attached on a specimen. Then, by using a gate circuit,[17] a certain echo was selected from echoes coming from the multiple reverberation in the specimen. The selected echo, which was not a single echo but actually a resultant pulse of a superposition of many echoes, was then amplified by a tuned amplifier[18] and fed to a lock-in amplifier.[19] On the other hand, the frequency synthesizer determining the carrier frequency was modulated externally by a low-frequency oscillator in the lock-in amplifier. Therefore, the input to the lock-in amplifier or the selected echo height was modulated by the low frequency f (40 Hz, for example).

When the superposition of the echoes was optimum, maximizing the echo height, the input signal contained only the $2f$ component giving the zero output of the lock-in amplifier. Furthermore, a feedback loop was set including a two-pen recorder[20] in order to record simultaneously the temperature of the specimen and the variation of the carrier frequency, which gives the zero output of the lock-in amplifier. This system was capable of detecting $\Delta V/V_0$ equal to 10^{-8} when the attenuation coefficient was not larger than about 0.2 dB/cm.

The procedure related to the temperature measurement, its stability, its gradient in the specimen, etc. were the same as were described in a previous paper.[8] The relative accuracy of the measured temperature was better than 0.001°K, and the absolute accuracy was about 0.02°K. The Néel temperature T_N of the present specimens were found to be (67.31±0.02)°K.

The present specimens were obtained from Semi Elements, Inc. Three pairs of the surfaces, with crystallographic orientations of (001), (100), and (110) were polished flat and parallel to each other. The surfaces were oriented within 0.5° from the above three principal directions by x ray. Rounding of the attenuation coefficient curve occurred only within 0.01°K of T_N in the log-log plot against $T-T_N$, which means that the specimens were nearly perfect.

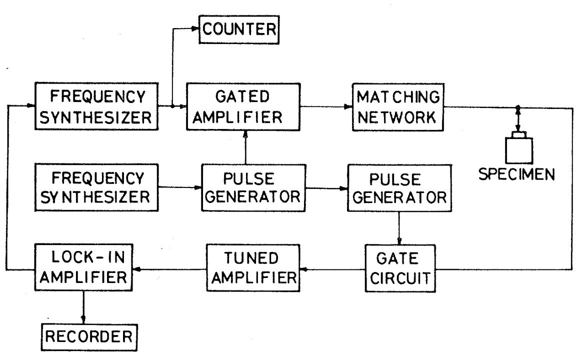

FIG. 1. Block diagram for the apparatus of sound-velocity measurement.

III. EXPERIMENTAL RESULTS

Figure 2 shows the observed dip of the sound velocity in MnF_2 near T_N for three kinds of the longitudinal waves. To discuss the anomalous part of the variation of the velocity of sound, the normal variation which would be expected if there were no phase change has to be determined. We employed here the simplest definition of the normal variation, that is, the normal variation can be given by a linear extrapolation of the sound-velocity change at temperatures far above T_N.

Figure 3 is, then, a log-log plot of the anomalous deviation of the velocity versus $T-T_N$ and $\epsilon\equiv|T-T_N|/T_N$ for $T>T_N$, and Fig. 4 is a similar plot for $T<T_N$. It is clear that there is no anisotropy in the critical exponent ζ which reminds us of the attenuation of sound experiment in MnF_2,[8] where there was also no orientation dependence of the critical exponent. This situation is also similar for the value of ζ for $T<T_N$, where the value is much smaller than that for $T>T_N$ for the velocity and the attenuation of the sound.

On the other hand, the magnitude of the anomalous variation of the sound velocity changes appreciably for different directions of the wave propagation; the variation is largest for $\mathbf{k}\|[001]$, and smallest for $\mathbf{k}\|[110]$. All of these variations are, however, not due to the anomalous thermal expansion[21] near the magnetic transition point, as the expansion anomaly is at most only 10^{-5}.

Figure 5 is a plot of $-\Delta V/V_0$ for two different frequencies for $T>T_N$, indicating that there does not seem to be any remarkable frequency dependence. Table I summarizes the observed result.

IV. THEORY OF SOUND-VELOCITY CHANGES

We here present a calculation of sound velocity in the presence of weak spin-phonon interaction as an

[11] H. J. McSkimin, J. Acoust. Soc. Am. **37**, 864 (1965).
[12] H. J. McSkimin and P. Andreatch, Jr., J. Acoust. Soc. Am. **41**, 1052 (1967).
[13] J. T. Holder (to be published).
[14] General Radio, Models 1163-A and 1164-A.
[15] Arenberg, Model PG-650C.
[16] Arenberg, Model WB-100SN.
[17] A combination of a number of General Radio's pulse generators (Model 1217C) and a homemade circuit.
[18] An amplifier built in MATEC's Model PR201.
[19] Princeton Applied Research, Model HR-8 with a preamplifier type C.
[20] Hewlett-Packard, Model 7100B.
[21] D. F. Gibbons, Phys. Rev. **115**, 1194 (1959).

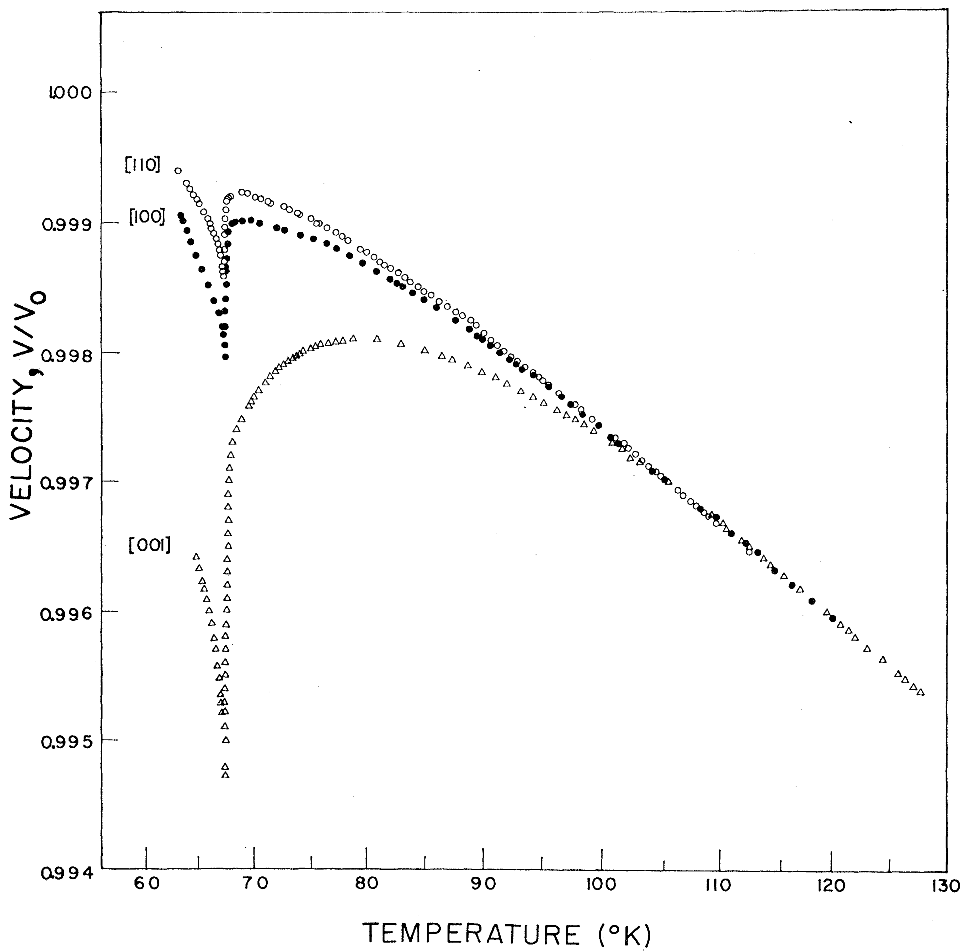

FIG. 2. Anomalous temperature dependence of measured velocities of 10-MHz longitudinal sound, propagating along three different directions.

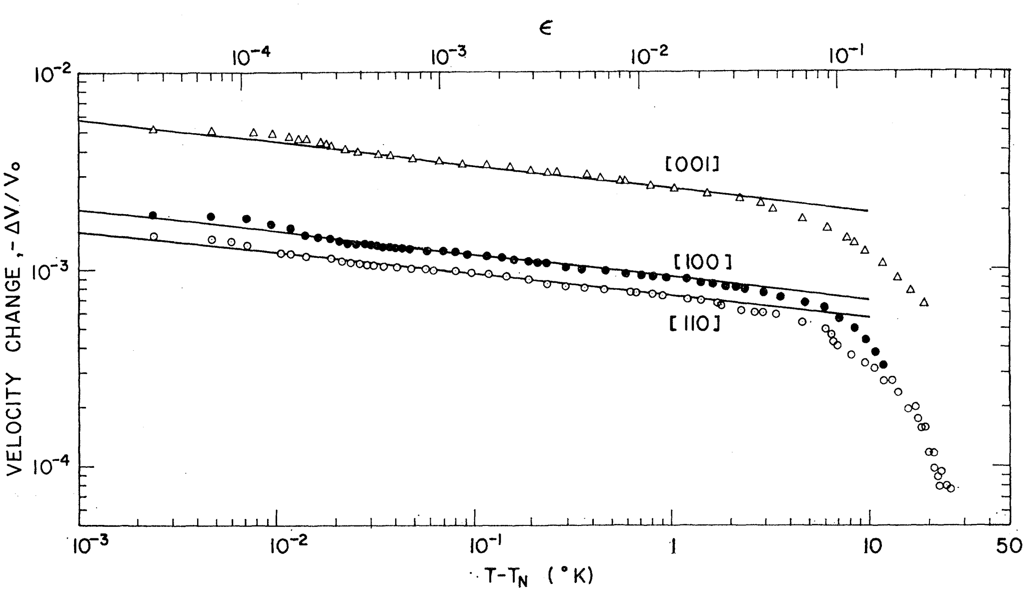

FIG. 3. A log-log plot of anomalous deviations of velocities of 10-MHz longitudinal sound above the Néel temperature.

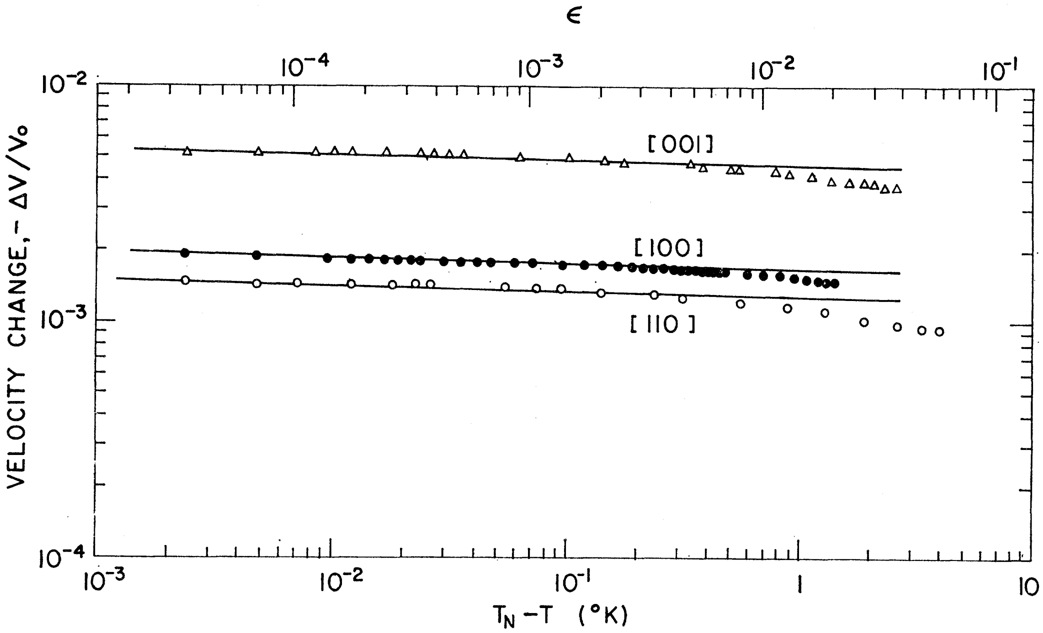

FIG. 4. A log-log plot of anomalous deviations of velocities of 10-MHz longitudinal sound below the Néel temperature.

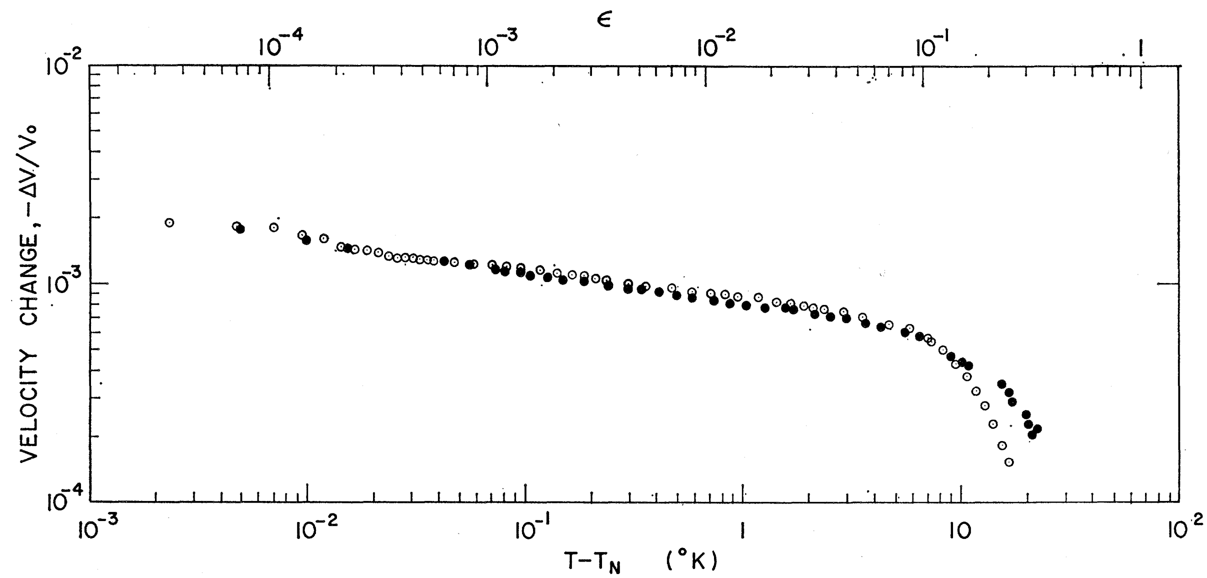

FIG. 5. A log-log plot of anomalous deviations of longitudinal sound velocities at different frequencies above the Néel temperature. ⊙, 10 MHz; ● 30 MHz.

TABLE I. Summary of the results.

k	Critical exponent ζ $T>T_N$	$T<T_N$	$\left(\frac{\Delta V}{V^{(0)}}\right)_{[k]} \Big/ \left(\frac{\Delta V}{V^{(0)}}\right)_{[110]}$	$(\Delta V\cdot V^{(0)})_{[k]}/(\Delta V\cdot V^{(0)})_{[110]}$
[110]	0.12	0.02	1	1
[100]	0.12	0.02	1.2$_6$	1.0$_2$
[001]	0.12	0.02	3.5$_5$	3.5$_5$

application of statistical-mechanical theory of collective motions at finite temperatures.[22] As long as we are interested in the critical anomaly in the sound wave due to magnetic transition, we may ignore lattice anharmonicity, and furthermore if there is no conserved quantity associated with the magnetic system,[23] the normal coordinates of the sound-wave mode are taken to be annihilation and creation operators of a sound-wave quantum $b_{\mathbf{k}}$ and $b_{\mathbf{k}}^*$.[24] Then the sound-wave frequency $\omega_{\mathbf{k}}$ is given by

$$\omega_{\mathbf{k}}=i(\dot{b}_{\mathbf{k}},b_{\mathbf{k}}^*)/(b_{\mathbf{k}},b_{\mathbf{k}}^*)=\langle[b_{\mathbf{k}},b_{\mathbf{k}}^*]\rangle/\hbar(b_{\mathbf{k}},b_{\mathbf{k}}^*)$$
$$=1/\hbar(b_{\mathbf{k}},b_{\mathbf{k}}^*),\qquad(4.1)$$

where

$$(A,B)\equiv\int_0^\beta d\lambda\langle Ae^{-\lambda H}Be^{\lambda H}\rangle,$$

the angular bracket denotes an ensemble average, H is the total Hamiltonian, and $\beta=1/k_BT$. The sound frequency shift that accompanies the sound-wave attenuation contributes only to sound-wave dispersion and does not affect the zero-frequency sound velocity, and we shall leave it out of consideration in this paper. For the system Hamiltonian H, we then take

$$H=H_0+H_1+H_2,\qquad(4.2)$$

where H_0 corresponds to uncoupled spin and phonon systems,

$$H_0=\sum_{\mathbf{k}}\hbar\omega_{\mathbf{k}}{}^0b_{\mathbf{k}}^*b_{\mathbf{k}}+\sum_\alpha\sum_{ij}J_{ij}{}^\alpha S_i{}^\alpha S_j{}^\alpha,\ \alpha=x,y,z,\qquad(4.3)$$

and the spin-phonon interaction Hamiltonians involving one and two phonons are given, respectively, by[24]

$$H_1=\sum_{\mathbf{k}}(\hbar/2NM\omega_{\mathbf{k}}{}^0)^{1/2}(b_{\mathbf{k}}+b_{-\mathbf{k}}{}^*)U_{\mathbf{k}}{}^{(1)},\qquad(4.4)$$

$$H_2=\sum_{\mathbf{k}}\sum_{\mathbf{k}'}(\hbar/2NM)(\omega_{\mathbf{k}}{}^0\omega_{\mathbf{k}'}{}^0)^{-1/2}(b_{\mathbf{k}}b_{-\mathbf{k}'}+b_{-\mathbf{k}}{}^*b_{\mathbf{k}'}{}^*$$
$$+b_{\mathbf{k}}b_{\mathbf{k}'}{}^*+b_{-\mathbf{k}}{}^*b_{-\mathbf{k}'})U_{\mathbf{k}\mathbf{k}'}{}^{(2)},\qquad(4.5)$$

$$U_{\mathbf{k}}{}^{(1)}=\sum_{ij}(e^{i\mathbf{k}\cdot\mathbf{R}_i}-e^{i\mathbf{k}_i\cdot\mathbf{R}_j})\mathbf{v}_{\mathbf{k}}\cdot\sum_\alpha\frac{\partial J_{ij}{}^\alpha}{\partial\mathbf{R}_i}S_i{}^\alpha S_j{}^\alpha,$$

$$U_{\mathbf{k}\mathbf{k}'}{}^{(2)}=\tfrac{1}{2}\sum_{ij}(e^{i\mathbf{k}\cdot\mathbf{R}_i}-e^{i\mathbf{k}\cdot\mathbf{R}_j})(e^{-i\mathbf{k}'\cdot\mathbf{R}_i}-e^{-i\mathbf{k}'\cdot\mathbf{R}_j})$$
$$\times\mathbf{v}_{\mathbf{k}}\mathbf{v}_{-\mathbf{k}'}:\sum_\alpha\frac{\partial^2J_{ij}{}^\alpha}{\partial\mathbf{R}_i\partial\mathbf{R}_j}S_i{}^\alpha S_j{}^\alpha,$$

where N is the number of lattice sites, M the mass per lattice site, $\mathbf{v}_{\mathbf{k}}$ the polarization vector of phonon $\mathbf{k}$, and $\mathbf{R}_i$ the position vector of ith site. Here we always assume that wave vectors such as $\mathbf{k}$ and $\mathbf{k}'$ also specify phonon polarizations. Our problem then amounts to calculating $(b_{\mathbf{k}},b_{\mathbf{k}}^*)$ regarding $H'\equiv H_1+H_2$ as a small perturbation. For this purpose we will make use of the following familiar expansion formulas:

$$\langle X\rangle=\langle X\rangle_0-\int_0^\beta d\lambda\langle H'(-i\hbar\lambda)X\rangle_0{}^{\mathrm{c}}+\int_0^\beta d\lambda_1\int_0^{\lambda_1}d\lambda_2$$
$$\times\langle H'(-i\hbar\lambda_1)H'(-i\hbar\lambda_2)X\rangle_0{}^{\mathrm{c}}+\cdots,$$

$$e^{-\lambda H}Xe^{\lambda H}=X(i\hbar\lambda)+\int_0^{\lambda_1}d\lambda_1[X(i\hbar\lambda),H'(i\hbar\lambda_1)]$$
$$+\int_0^\lambda d\lambda_1\int_0^{\lambda_1}d\lambda_2[[X(i\hbar\lambda),H'(i\hbar\lambda_1)]H'(i\hbar\lambda_2)]$$
$$+\cdots,\qquad(4.6)$$

where $X(i\hbar\lambda)\equiv e^{-\lambda H_0}Xe^{\lambda H_0}$ for any X, $\langle\cdots\rangle_0$ is the unperturbed ensemble average, and $\langle ABC\cdots\rangle_0{}^{\mathrm{c}}$ is the cumulant or connected average of the product of A, B, C, $\cdots$. Then we find, up to the second order in H', that for any A and B,

$$(A,B)=\int_0^\beta d\lambda\langle AB(i\hbar\lambda)\rangle_0-\int_0^\beta d\lambda_1\int_0^\beta d\lambda_2\langle H'(-i\hbar\lambda_1)\{AB(i\hbar\lambda_2)\}\rangle_0{}^{\mathrm{c}}+\int_0^\beta d\lambda_1\int_0^{\lambda_1}d\lambda_2\langle A[B(i\hbar\lambda_1),H'(i\hbar\lambda_2)]\rangle_0$$
$$+\int_0^\beta d\lambda_1\int_0^{\lambda_1}d\lambda_2\int_0^{\lambda_2}d\lambda_3\langle A[[B(i\hbar\lambda_1),H'(i\hbar\lambda_2)],H'(i\hbar\lambda_3)]\rangle_0$$
$$-\int_0^\beta d\lambda_1\int_0^\beta d\lambda_2\int_0^{\lambda_1}d\lambda_3\langle H'(-i\hbar\lambda_2)\{A[B(i\hbar\lambda_1),H'(i\hbar\lambda_3)]\}\rangle_0{}^{\mathrm{c}}$$
$$+\int_0^\beta d\lambda_1\int_0^\beta d\lambda_2\int_0^{\lambda_2}d\lambda_3\langle H'(-i\hbar\lambda_2)H'(-i\hbar\lambda_3)\{AB(i\hbar\lambda_1)\}\rangle_0{}^{\mathrm{c}},\qquad(4.7)$$

[22] H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965).
[23] Spin-lattice relaxation would be enough to guarantee this. If this were not the case, $b_{\mathbf{k}}$ and $b_{\mathbf{k}}^*$ would couple with such conserved quantities to form normal coordinates.
[24] K. Tani and H. Mori, Progr. Theoret. Phys. (Kyoto) **39**, 876 (1968); and (private communications).

where the quantities in curly brackets should be treated as single units in taking cumulant averages.

Choosing $A=b_{\mathbf{k}}$ and $B=b_{\mathbf{k}}^*$, the rest of the calculation is straightforward, and only the results will be presented. Here we retain only the lowest-order non-vanishing contributions, i.e., H_1 and H_2 appear in the second- and first-order perturbations, respectively. The frequency shift $\Delta\omega_{\mathbf{k}}$ can then be written as

$$\Delta\omega_{\mathbf{k}}=(\Delta\omega_{\mathbf{k}})_1+(\Delta\omega_{\mathbf{k}})_2\,, \tag{4.8}$$

where

$$(\Delta\omega_{\mathbf{k}})_1\equiv-(\beta/2NM\omega_{\mathbf{k}}^0)\langle U_{\mathbf{k}}^{(1)}U_{-\mathbf{k}}^{(1)}\rangle_0\,, \tag{4.9}$$

$$(\Delta\omega_{\mathbf{k}})_2\equiv\frac{1}{2NM\omega_{\mathbf{k}}^0}\langle U_{\mathbf{k}\mathbf{k}}^{(2)}\rangle_0\left(1+\frac{\beta\hbar\omega_{\mathbf{k}}^0}{e^{\beta\hbar\omega_{\mathbf{k}}^0}-1}\right). \tag{4.10}$$

Here we have used the fact that for crystals with inversion symmetry,

$$\langle U_{\mathbf{k}\mathbf{k}}^{(2)}\rangle_0=+\langle U_{-\mathbf{k}-\mathbf{k}}^{(2)}\rangle_0$$

and

$$\langle U_{\mathbf{k}}^{(1)}U_{-\mathbf{k}}^{(1)}\rangle_0=\langle U_{-\mathbf{k}}^{(1)}U_{\mathbf{k}}^{(1)}\rangle_0\,.$$

The change in the velocity of sound, $\Delta V_{\mathbf{k}_0}$ is

$$\Delta V_{\mathbf{k}_0}=\lim_{k\to0}\Delta\omega_{\mathbf{k}}/k=\Delta V_{\mathbf{k}_0}^{(1)}+\Delta V_{\mathbf{k}_0}^{(2)}\,, \tag{4.11}$$

with

$$\Delta V_{\mathbf{k}_0}^{(1)}\equiv-(\beta/2NMV_{\mathbf{k}_0}^0)\langle(\delta W_{\mathbf{k}_0}^{(1)})^2\rangle\,, \tag{4.12}$$

$$\Delta V_{\mathbf{k}_0}^{(2)}\equiv(2NMV_{\mathbf{k}_0}^0)^{-1}\langle W_{\mathbf{k}_0}^{(2)}\rangle_0\,, \tag{4.13}$$

where

$$W_{\mathbf{k}_0}^{(1)}\equiv\sum_{ij}\mathbf{k}_0\cdot\mathbf{R}_{ij}\mathbf{v}_{\mathbf{k}}\cdot\sum_{\alpha}\frac{\partial J_{ij}^{\alpha}}{\partial\mathbf{R}_i}S_i^{\alpha}S_j^{\alpha}\,, \tag{4.14}$$

$$W_{\mathbf{k}_0}^{(2)}\equiv\sum_{ij}(\mathbf{k}_0\cdot\mathbf{R}_{ij})^2\mathbf{v}_{\mathbf{k}}\mathbf{v}_{-\mathbf{k}}:\sum_{\alpha}\frac{\partial^2 J_{ij}^{\alpha}}{\partial\mathbf{R}_i\partial\mathbf{R}_j}S_i^{\alpha}S_j^{\alpha}\,, \tag{4.15}$$

and

$$\mathbf{k}_0\equiv\mathbf{k}/k\,,\quad \mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j\,,\quad\text{and}\quad \delta X\equiv X-\langle X\rangle_0$$

for any X. $V_{\mathbf{k}_0}^{(0)}$ is the sound velocity in the absence of spin-phonon interaction, which still depends upon the direction of propagation of sound as well as on the polarization, which we indicate by the subscript $\mathbf{k}_0$.

The results show that anomalous changes in sound velocity are expressed in terms of two-spin and four-spin correlation functions. Now, as far as the critical anomaly is concerned, the $W_{\mathbf{k}}$'s behave as the spin Hamiltonian and $-\Delta V_{\mathbf{k}_0}^{(1)}$ has an anomalous peak which behaves like the specific heat, and $\Delta V_{\mathbf{k}_0}^{(2)}$ behaves like the internal energy of the spin system. Thus, when $\Delta V_{\mathbf{k}_0}^{(1)}\neq0$, this contribution dominates. However, there are also the cases where $\Delta V_{\mathbf{k}_0}^{(1)}=0$ and $\Delta V_{\mathbf{k}_0}$ behaves like $\Delta V_{\mathbf{k}_0}^{(2)}$.[25] In the following, we assume that $\Delta V_{\mathbf{k}_0}^{(1)}\neq0$ as the present experiment indicates and also restrict ourselves to the longitudinal sound waves $\mathbf{v}_{\mathbf{k}}=\mathbf{k}_0$. Thus we have

$$W_{\mathbf{k}_0}^{(1)}=\sum_{ij}\sum_{\alpha\gamma\delta}\hat{k}_\gamma\hat{k}_\delta R_{ij\gamma}J_{ij\delta}^{\alpha}S_i^{\alpha}S_j^{\alpha}\,,\quad \gamma,\delta=x,y,z\,, \tag{4.16}$$

with $J_{ij\delta}^{\alpha}\equiv\partial J_{ij}^{\alpha}/\partial R_{ij\delta}$, and $R_{ij\delta}$ is the component of $\mathbf{R}_{ij}$ along the δ axis.

Let us now turn to the contributions of various neighboring spin pairs to $\Delta V_{\mathbf{k}_0}^{(1)}$ for isotropic Heisenberg magnets $J_{ij}^x=J_{ij}^y=J_{ij}^z=J_{ij}$. If one factorizes the four spin correlations into the product of spin pair correlations,

$$-\Delta V_{\mathbf{k}_0}^{(1)}\propto F_{\mathbf{k}_0}^{(2)}/V_{\mathbf{k}_0}^0\,, \tag{4.17}$$

aside from a common factor that becomes singular at T_N, where

$$F_{\mathbf{k}_0}=\sum_{j}\sum_{\gamma\delta}\hat{k}_\gamma\hat{k}_\delta R_{ij\gamma}J_{ij\delta}\,. \tag{4.18}$$

Thus, the relative importance of various neighboring spin pairs to $-\Delta V_{\mathbf{k}_0}^{(1)}$ is found from $F_{\mathbf{k}_0}$. Now, the factorization approximation is known to be rather poor, overestimating the singularity at T_N, and hence the relative importance of various neighboring spin pairs would, in general, differ from that given by (4.17) and (4.18). However, in many magnetic substances, the exchange interactions between particular pairs of neighboring spins (for MnF_2, second-neighbor pairs) give the largest contribution to $-\Delta V_{\mathbf{k}_0}^{(1)}$, and if we assume that the correlation of exchange energy density fluctuations associated with these particular neighbors does not depend on the orientation of these neighboring pairs, as long as the distance between these pairs is very large,[26] the relative importance of various pairs of this kind is correctly given by $F_{\mathbf{k}_0}$. Although the relative importance of contributions to $-\Delta V_{\mathbf{k}_0}^{(1)}$ involving other kinds of spin pairs are no longer given correctly by $F_{\mathbf{k}_0}$ the discrepancy would still amount to finite multiplicative factors of order unity, because all sorts of four spin correlations involved in $\langle(W_{\mathbf{k}_0}^{(1)})^2\rangle$ would produce similar singular factors, which behave like specific heat (see below). Thus, we may still use $F_{\mathbf{k}_0}$ to obtain rough estimates of the contributions of other

[25] For instance, when spins are arranged in a simple cubic lattice with only nearest-neighbor exchange interactions, a shear wave with $\mathbf{k}$ along [100] and $\mathbf{v}_{\mathbf{k}}$ along [010] has vanishing $\Delta V_{\mathbf{k}_0}^{(1)}$. Rénard and Garland [J. Chem. Phys. **44**, 1125 (1966)] also mention such an example for a two-dimensional lattice. They also note that the compressional stiffness constant behaves like specific heat. Our result thus may be viewed as a generalization of Rénard and Garland's result. The results similar to (4.11)–(4.15) have been previously obtained also by V. N. Kashcheev [Phys. Letters **25A**, 71 (1967)]. We are indebted to Professor B. Lüthi for bringing this reference to our attention.

[26] For the square Ising model with nearest-neighbor interaction, this has been verified to be the case for nearest-neighbor spins at the critical point T_c. The energy-density–energy-density correlation at a distance R, $f_{\mathrm{EE}}(R)$, has the form $(J\sinh 2K_c'+J')^2\times$(singular factor at T_c), where J and J' are the exchange interactions of horizontal and vertical spin pairs and $K_c'=J'/k_BT_c$ [R. J. Hecht, Ph.D. thesis, University of Illinois, 1967 (unpublished); Phys. Rev. **158**, 557 (1967)]. Correlation of two spin pairs of various orientations are given as the coefficients of J^2, $2JJ'$, and J'^2 of $f_{\mathrm{EE}}(R)$. Since $\sinh 2K_c'\to1$ as $J\to J'$, these correlations become identical when $J=J'$ and $T=T_c$.

kinds of pairs to $-\Delta V_{\mathbf{k}_0}{}^{(1)}$. Thus, we calculated $F_{\mathbf{k}_0}$ for various longitudinal sound waves for the body-centered tetragonal magnetic lattice like MnF_2 with the lattice constants a and c. Abbreviating $J_{n\delta}'$ for $\partial J_{ij}/\partial R_{ij\delta}$ with $\mathbf{R}_{ji}$ the position vector for the nth neighbor in the first quadrant as shown in Fig. 6, we obtain the following results for $F_{\mathbf{k}_0}$ (note that $J_{3y}'=0$ and $J_{2x}'=J_{2y}'$ by symmetry):

$$\begin{aligned} &\mathbf{k}\text{ along }[100]\text{ or }[010], && 2a(2J_{2x}'+J_{3x}') \\ &\mathbf{k}\text{ along }[001], && 2c(2J_{2z}'+J_{1z}') \qquad (4.19)\\ &\mathbf{k}\text{ along }[110], && 2a(2J_{2x}'+J_{3x}'). \end{aligned}$$

The same quantities appear in the static correlation of random force in the work of Tani and Mori.[24]

The factorization approximation used to obtain (4.17), (4.18), and (4.19) can be replaced by more modest assumptions for four-spin correlations to obtain a slightly more complicated but equally useful result for $\langle (W_{\mathbf{k}_0}{}^{(1)})^2\rangle$. For the magnetic system being considered here, we find for $W_{\mathbf{k}_0}{}^{(1)}$ the following:

for $\mathbf{k}$ along [100],

$$a\sum_i\left[\tfrac{1}{2}J_{2x}'\sum_{\Delta_2}^{8}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_2}+J_{3x}'\sum_{\Delta_3^x\neq 0}^{2}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_3}\right],$$

for $\mathbf{k}$ along [001],

$$c\sum_i\left[\tfrac{1}{2}J_{2z}'\sum_{\Delta_2}^{8}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_2}+J_{1z}'\sum_{\Delta_1}^{2}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_1}\right], \qquad (4.20)$$

for $\mathbf{k}$ along [110],

$$\tfrac{1}{2}a\sum_i\left[2J_{2x}'\sum_{\Delta_2,\Delta_2^x\Delta_2^y>0}^{4}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_2}+J_{3x}'\sum_{\Delta_3}^{4}\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_3}\right],$$

where $\mathbf{\Delta}_n$ is $\mathbf{R}_{ij}$ for the nth neighbor spin pairs. If we only assume that the correlation of two spin pairs does not depend upon the orientation of two spin sites in individual pairs[27] and that they all show the same type of singularity at T_N when the distance between the two pairs is very large, we have, instead of $F_{\mathbf{k}_0}{}^2$, the corresponding quantity $\tilde{F}_{\mathbf{k}_0}{}^2$ of the following forms, which give the relative importance of various neighboring spin pairs to $-\Delta V_{\mathbf{k}_0}{}^{(1)}$:

for $\mathbf{k}$ along [100],

$$(2a)^2[(2J_{2x}')^2+2(2J_{2x}')J_{3x}'f_{23}+(J_{3x}')^2f_{33}],$$

for $\mathbf{k}$ along [001],

$$(2c)^2[(2J_{2z}')^2+2(2J_{2z}')J_{1z}'f_{12}+(J_{1z}')^2f_{11}], \qquad (4.21)$$

for $\mathbf{k}$ along [110],

$$(2a)^2[(2J_{2x}')^2+2(J_{2x}')J_{3x}'f_{23}+(J_{3x}')^2f_{33}],$$

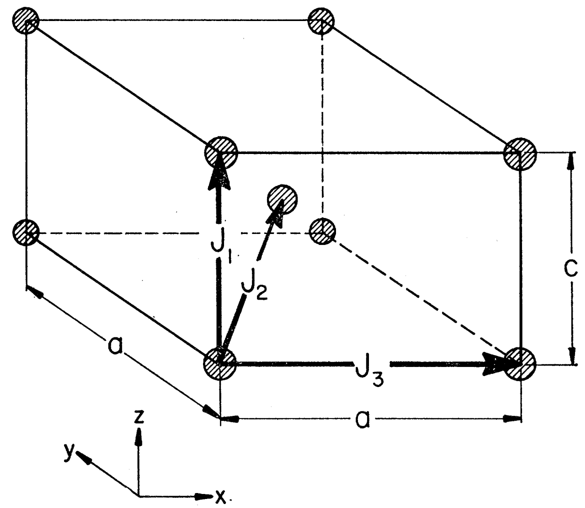

FIG. 6. A unit cell of MnF_2. First-, second-, and third-neighbor exchange interactions are indicated by J_1, J_2, and J_3, respectively.

where

$$f_{mn}\equiv\sum_{\mathbf{R}}\varphi_{mn}(\mathbf{R})/\sum_{\mathbf{R}}\varphi_{22}(\mathbf{R}),$$

$$\text{(independent of the orientation of }\mathbf{\Delta}_m\text{ and }\mathbf{\Delta}_n) \qquad (4.22)$$

with

$$\varphi_{mn}(\mathbf{R})=\langle\delta(\mathbf{S}_i\cdot\mathbf{S}_{i+\Delta_m})\delta(\mathbf{S}_{i+\mathbf{R}}\cdot\mathbf{S}_{i+\mathbf{R}+\Delta_n})\rangle. \qquad (4.23)$$

The magnitudes of $-\Delta V_{\mathbf{k}_0}{}^{(1)}$ are then proportional to $\tilde{F}_{\mathbf{k}_0}{}^2/V_{\mathbf{k}_0}{}^{(0)}$. Equation (4.19) further supposes that $f_{23}=f_{12}=f_{11}=f_{33}=1$. These f's reduce to finite numbers of order unity at T_N and do not depend on the orientation of $\mathbf{\Delta}$'s by our assumptions.

On the basis of these results we shall discuss in Sec. V our experimental results for $\Delta V_{\mathbf{k}_0}$.[28]

V. DISCUSSION

The first point to be mentioned is the value of the critical exponent ζ in Eq. (1.1). The present experiment revealed that ζ is 0.12 in the paramagnetic phase, which

[27] This applies, of course, only when the change of orientation of pairs does not alter the distance between the two sites of the pair. Thus, for a first neighboring pair, only one orientation is possible. Similarly, for a third neighboring pair, only two orientations are possible, and so on. Our assumption can be visualized also as follows: The four-spin correlations of our interest can be viewed as a change in correlation of neighboring spin pairs due to a disturbance caused by a slight change in an exchange interaction between another neighboring spin pair situated a long distance away.

Our assumption is then true if a local disturbance propagates through the lattice of MnF_2 in circularly symmetrical fashion in the (001) plane at large distance as the critical point is approached. This is similar to the way that waves on a water surface produced by a thrown stone of irregular shape propagate in a circularly symmetric manner at large distance.

[28] After a substantial part of this work was completed, we found that H. S. Bennett appears to have done a similar calculation, which was quoted by Moran and Lüthi (Ref. 4). Since the details of this work are not yet available to us, we cannot compare his work with ours except to emphasize that in our final result (4.21) we have not used the factorization approximation of four-spin correlations, which apparently was used by Bennett.

is in agreement with the corresponding exponent α for the specific heat, that is $0\lesssim\alpha\lesssim0.16$.[29] Furthermore, from the acoustic experiment, ζ is 0.02 in the antiferromagnetic phase, which also seems to agree with α in the antiferromagnetic phase, where $0\lesssim\alpha\lesssim0.18$.[29] The conclusion expressed by Eq. (4.11) and the discussion that follows was, thus, proved to be valid by the present experiment.

The present theory can also explain relative magnitudes of the anomalous change in the sound velocity for different directions of the wave propagation. First of all, the theory accounts for the fact that $(\Delta V\cdot V^{(0)})_{[110]}$ is very close to $(\Delta V\cdot V^{(0)})_{[100]}$, since the expressions for $F_{\mathbf{k}_0}{}^2$ and $\tilde{F}_{\mathbf{k}_0}{}^2$ are exactly the same up to J_3' for these longitudinal waves implying that $V_{\mathbf{k}_0}{}^{(0)}\cdot\Delta V_{\mathbf{k}_0}{}^{(1)}$ should be the same for them by (4.17).[30] In Table I, the magnitude of $(\Delta V\cdot V^{(0)})_{[\mathbf{k}]}$, which is proportional to $F_{\mathbf{k}_0}{}^2$ or $\tilde{F}_{\mathbf{k}_0}{}^2$, is compared, and the conclusion is verified there. This gives a rather direct support to our theory of Sec. IV. Furthermore, the relative magnitude of $\Delta V\cdot V^{(0)}$ for [110] and [001] gives us the relative value of the derivative of the exchange interaction J'. Neglecting the supposedly small quantities, J_1' and J_3', we can deduce that

$$|J_{2z}'/J_{2x}'|=2.7_7\,, \tag{5.1}$$

which agrees rather well with the value, 2.2∼2.6, obtained from the attenuation measurement in the same specimens.[9] The present value is considered to be more reliable because the sound velocity is more simply related to the spin-phonon interaction, not involving relaxation times. The present value is also in a good agreement with the value 2.1, deduced by Tani and Mori[24] from the experiment by Benedek and Kushida.[31]

The relaxation time should also be discussed here. Assuming a single effective relaxation time τ, the ratio of the attenuation coefficient α^* to the sound-velocity change gives τ [22,32]

$$\tau=(V^0/\omega^2)[\alpha^*/(-\Delta V/V_0)]. \tag{5.2}$$

Using the values of α^* and $-\Delta V/V_0$ at $\epsilon=10^{-3}$ for 10 MHz, this formula yields $\tau=2.9\times10^{-9}$ sec, which means that $\omega\tau$ becomes unity for frequencies of about 60 MHz. Therefore, in the frequency region of our experiment, $\omega\tau\sim1$, which makes the interpretation of the experimental results somewhat difficult. Thus, much insight will be gained into the sound propagation mechanism in MnF_2 by acoustic measurements at high frequencies $\omega\gg1/\tau$ and at low frequencies $\omega\ll1/\tau$ where $\alpha^*\propto\omega^2$.

Let us now consider further consequences and implications of the existence of such a relaxation time. For this purpose we need another relaxation time τ_c that characterizes the dynamics of critical fluctuations.

In the absence of magnetocrystalline anisotropy, we put[33]

$$\tau_c^{-1}=\omega_\infty\epsilon\,, \tag{5.3}$$

where ω_∞ is the characteristic frequency far from T_N. We estimate ω_∞ from the second frequency moment of the staggered magnetization σ at infinite temperature as

$$\omega_\infty{}^2=\langle\dot{\sigma}^2\rangle_\infty/\langle\sigma^2\rangle_\infty=(2^7/3)S(S+1)J_2{}^2. \tag{5.4}$$

For $S=\frac{5}{2}$ and $|J_2|=1.76$°K,[34] we found that $\omega_\infty=4.5\times10^{12}$ sec^{-1}. In the presence of a small uniaxial anisotropy such as in MnF_2, τ_c^{-1} would behave as ϵ^γ in the immediate vicinity of T_N [33] and as ϵ for temperatures further away, where $\gamma\approx\frac{4}{3}$ is the critical exponent for staggered susceptibility. Both of these behaviors may be represented by a single formula for τ_c^{-1}:

$$\tau_c^{-1}=\omega_\infty\epsilon^\gamma(\epsilon_A+\epsilon)^{1-\gamma}\,, \tag{5.5}$$

where ϵ_A is a small number representing the importance of anisotropy energy compared to the exchange energy, and we take $\epsilon_A=H_A/H_E$. Here, H_A is the anisotropy field of 7800 G, and H_E is the exchange field of 550 000 G for MnF_2,[35] and we have $\epsilon_A=1.4\times10^{-2}$.

Suppose that the spin-phonon interaction Hamiltonian H' is divided into two parts, $H'=H_a+H_b$, such that the two relaxation times τ_a and τ_b associated with H_a and H_b, respectively, exhibit distinct behavior near the transition point. Then the attenuation coefficient α^* is proportional to $\langle H_a{}^2\rangle\tau_a+\langle H_b{}^2\rangle\tau_b$.[36] Thus, if $\langle H_a{}^2\rangle$ and $\langle H_b{}^2\rangle$ are of the same order of magnitudes, the attenuation coefficient is dominated by the process with longer relaxation time.[37] In the following discussion we assume that the two relaxation times τ and τ_c somehow correspond to τ_a and τ_b.

Now, $\tau=\tau_c$ for $\epsilon\equiv\epsilon_0\approx3\times10^{-4}$, i.e., $|\Delta T|=|T-T_N|\equiv|\Delta T_0|\approx(2\times10^{-2})$°K. For $|\Delta T|\gtrsim|\Delta T_0|$, $\tau>\tau_c$ and the relaxation processes associated with τ are expected to dominate the attenuation of sound at least for small

[29] L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967).

[30] $\Delta V\cdot V^{(0)}$ considered here may be written as $\Delta(\frac{1}{2}V^2)$. This quantity arises from the "polarization operator" that appears in the phonon Green's function. See for instance, H. Wagner [report of work prior to publication (1969)].

[31] G. B. Benedek and T. Kushida, Phys. Rev. **118**, 46 (1960).

[32] Although, strictly speaking, this formula is valid for $\omega\tau\ll1$, where $\alpha^*\propto\omega^2$ because the major contribution to ΔV comes from the first-moment sound-wave frequency which does not depend on the frequency ω, the formula still gives the correct order of magnitude of τ for larger $\omega\tau$ unless $\omega\tau\gg1$.

[33] K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **39**, 285 (1968); **40**, 11 (1968); B. Halperin and P. C. Hohenberg, Phys. Rev. **177**, 952 (1968); J. Villain, J. Phys. (Paris) **29**, 687 (1968); P. Résibois, J. Phys. Soc. Japan Suppl. **26**, 127 (1969).

[34] A. Okazaki, K. C. Turberfield, and R. W. H. Stevenson, Phys. Letters **8**, 9 (1964).

[35] S. Foner, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. I, p. 383.

[36] An example of this is the case where H_a is identical to the spin-system Hamiltonian apart from a constant numerical factor, and H_b is the remainder. The separation of H' into H_a and H_b can be conveniently made by the use of the projection operator. See Ref. 39.

[37] This case should not be confused with the case where more than one processes compete to relax the same part of the spin-phonon interaction Hamiltonian. In the latter case, of course, the relaxation process with the shortest relaxation time is most important.

sound-wave frequencies ω, such that $\omega\tau \lesssim 1$. For $|\Delta T| \lesssim |\Delta T_0|$, on the other hand, the relaxation processes associated with τ_c dominate the sound attenuation for $\omega \lesssim 1/\tau_c$. Thus, the attenuation changes its behavior at $|\Delta T| \simeq 0.02°K$ at least for $\omega \lesssim 1/\tau$ and also the curve of attenuation versus temperature changes its character at the frequency $\omega \sim 1/\tau \approx 55$ MHz. Indeed the attenuation data reported elsewhere by one of the present authors (A.I.) appear to exhibit just such a behavior.[8]

Our discussion so far suggests the existence of two relaxation times, τ and τ_c. The question then arises that these two relaxation times should appear in other experiments such as NMR linewidth and neutron scattering.[38] In order to fully answer this question, we must know the nature of the relaxation process that has this characteristic time, which is not known. We merely point out that NMR linewidth and neutron scattering directly involve time-displaced pair-correlation functions of the order parameter,[38] hence the relaxation process entering these experiments have a characteristic time τ_c. However, these experiments do not involve processes associated with energy change of the spin system, for instance. On the other hand, the fact that the attenuation of sound involves four-spin time correlation function provides room for processes other than just the order parameter relaxation[39] and, thus, furnishes a tool for investigating such relaxation phenomena, a feature also shared by inelastic light scattering experiment.[40] Thus, the interpretation of propagation experiments of sound is, in general, more difficult than those of NMR and neutron. Nevertheless, under certain special circumstances, the interpretation can be made as simple. We illustrate the point by considering the attenuation of sound in an ideal cubic magnet, such as $RbMnF_3$, where only the nearest-neighbor spins are exchange-coupled.[41] Then for a longitudinal wave propagating along [111] direction, all the exchange interactions contribute equally to spin-phonon interactions, and only the relaxation of spin energy density affects the propagation of sound. This is not always the case for other directions of sound propagation.[42]

[38] P. Heller, Rept. Progr. Phys. **30**, 731 (1967); W. Marshall and R. D. Lowde, *ibid.* **31**, 705 (1968).

[39] K. Kawasaki, Phys. Letters **29A**, 406 (1969).

[40] P. A. Fleury, Phys. Rev. **180**, 591 (1969); T. Moriya, J. Phys. Soc. Japan **23**, 490 (1967).

[41] C. G. Windsor and R. W. H. Stevenson, Proc. Phys. Soc. (London) **87**, 501 (1966).

VI. CONCLUDING REMARKS

In the present paper, we reported the detailed measurements of anomalous sound-velocity changes of MnF_2 near the Néel point. The results support a theory based on weak spin-phonon coupling of the forms (4.4) and (4.5) and yield a useful information for the spacial derivatives of exchange interaction (5.1). The results are then combined with sound-attenuation data in order to investigate the absorption mechanism at sound, which suggests the existence of a rather long relaxation time of 2.9×10^{-9} sec. Although the nature of the relaxation processes with such long relaxation time is not yet clear, the finding warrants further experimental and theoretical investigations on this point, which we hope will eventually solve mysteries besetting the propagation of sound near magnetic critical points.

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[42] A similar point has been discussed by Tani and Mori (Ref. 24) for MnF_2. Recently, Lüthi and Pollina (Ref. 5) observed that their sound-propagation data are consistent with the assumption that spin-phonon coupling is proportional to the energy density of spin system. In fact, however, in their experimental situation, the relaxation of total energy density of spins as well as the relaxations of various parts of spin energy density associated with exchange interactions of spin pairs in various directions play a role. Their results show that the latter relaxation processes do not produce any critical anomaly, which still remains to be understood theoretically.