Spin-Lattice Relaxation near the Critical Point: $RbMnF_3$, MnF_2, EuO†

D. L. Huber
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
(Received 17 August 1970)

Electronic spin-lattice relaxation in disordered ferro- and antiferromagnets is discussed with particular emphasis on the region near the critical point. A general expression for the relaxation time is derived. The time it takes for the spins to come to thermal equilibrium with the lattice is directly proportional to the magnetic specific heat, as anticipated from thermodynamic arguments. It is shown that systems whose ordering temperature is at least comparable to the peak in the density of states of the acoustic-phonon modes can have very short relaxation times. This happens because the spins can interact with essentially all the acoustic modes. Relaxation times are estimated for three systems: $RbMnF_3$, MnF_2, and EuO. The implication of these results for the interpretation of ultrasonic attenuation measurements is discussed. It is found that the calculated values for the relaxation times agree qualitatively with the values inferred from ultrasonic data for $RbMnF_3$. The behavior of EuO is analyzed. We find that our values of T_1 are compatible with the dominance of the spin-lattice mechanism in the decay of the energy-density fluctuations with wavelengths comparable to the wavelengths of the ultrasonic phonons.

I. INTRODUCTION

Studies of ultrasonic attenuation in magnetic systems in the vicinity of a second-order phase transition have provided unique insight into the critical dynamics of the spin system.[1-5] Because the coupling to the sound wave involves terms which are quadratic in the spin operators, ultrasonic measurements are a probe of the dynamics of the four-spin correlation functions. This is in contrast to the neutron-scattering experiments which directly probe the two-spin functions.

According to current interpretations, a variety of experimental results can be explained by assuming that the interaction which is responsible for the attenuation can be separated into two parts.[6,7] The combination of spin operators associated with the first part has a dynamical behavior which is characteristic of the fluctuations in the energy density. This is in contrast to the second part where the dynamics is governed by the fluctuations in the order parameter. Ultrasonic attenuation in rare-earth metals is attributed to the order-parameter term.[8] On the other hand, the weak or nonexistent divergences in the attenuation in the insulators EuO, $RbMnF_3$, and MnF_2 have been explained by postulating the dominance of the energy-density term. This dominance is believed to be connected with range of the exchange interaction, which in insulators is limited primarily to nearest neighbors.

In particular, the absence of a divergence in the attenuation in the ferromagnet EuO has been explained by assuming that the long-wavelength energy fluctuations obey a diffusion equation where the diffusion constant is written as the ratio of the thermal conductivity of the spin system to the magnetic specific heat.[9] The weak temperature dependence of the attenuation was interpreted as mirroring a correspondingly weak temperature dependence in the thermal conductivity. Such an interpretation is supported by theoretical studies which suggest that the thermal conductivity remains finite as the critical temperature is approached from above.[10,11]

The weak but measurable singularity in the attenuation in the antiferromagnets $RbMnF_3$ and MnF_2 is believed to have a different origin. It has been pointed out that the anomalous behavior may reflect the existence of a nondiffusive decay process for the energy fluctuations.[7] In particular, Kawasaki has suggested that the dynamics of the long-wavelength fluctuations may be governed by the spin-lattice relaxation time.[12] If the relaxation time is proportional to the magnetic specific heat, as predicted by thermodynamic arguments, then the attenuation will vary as the square of the specific heat. Recently, Gorodetsky *et al.* have measured the attenuation in $RbMnF_3$ and have found the predicted C_H^2 behavior.[13] Moreover, by studying the frequency dependence of the attenuation they have been able to infer values for the relaxation time. These turn out to be on the order of 10^{-10} sec.

The behavior of MnF_2 is somewhat more complicated. The authors of Ref. 7 have interpreted their results by assuming roughly comparable order-parameter and energy-fluctuation terms.[14] For $T - T_N \lesssim 2\times10^{-2}$ °K the order-parameter fluctuations dominate, while outside this region energy fluctuations are important. By measuring the ratio of the attenuation to the change in sound velocity they were also able to estimate the relaxation time. They found a value on the order of 3×10^{-9} sec.

The purpose of this paper is to examine the spin-lattice relaxation process in magnetic insulators in the immediate vicinity of the critical point. In par-

ticular, we will attempt to account for the fast relaxation times in $RbMnF_3$ and MnF_2 which are in distinct contrast to the slow relaxation time which must be invoked to explain the attenuation in EuO.

The remainder of the paper is divided into three parts. In the first part we develop the formalism necessary to calculate the relaxation time near the critical point, while in the second part we consider in detail the three magnetic insulators mentioned above. The significance of our findings is discussed in Sec. IV.

II. FORMAL CALCULATION

Our understanding of spin-lattice relaxation in dilute paramagnetic salts is quite thorough.[15,16] The coupling of the spin system to the crystal lattice is primarily through the orbit-lattice interaction which arises from the strain dependence of the crystalline field. At low temperatures the relaxation involves the absorption and emission of phonons whose energies match the separations between the levels of the spin system. At higher temperatures multiphonon or Raman processes become important.

To our knowledge, relaxation processes near the critical point have not been studied in detail either experimentally or theoretically. The calculation of the relaxation time in the critical region differs in two important ways from the corresponding calculation for magnetically dilute systems. First, we are dealing with a spin system whose level structure and dynamics are not known in detail. Second, besides the orbit-lattice interaction the phonons can couple to the spins through the strain dependence of the exchange interaction. This latter coupling is especially important when the magnetic ions are in orbital s state, where the orbit-lattice interaction is especially weak.[17]

In the paragraphs to follow, we will outline a formal calculation of the spin-lattice relaxation time. The expression for the relaxation time will be evaluated in several limiting cases. In the course of the analysis we will make a number of simplifying approximations. Some of these pertain to the lattice and can be readily improved upon; others, which are more crucial, pertain to the dynamics of the spin system. These we will discuss in detail.

In the present context, we identify the spin-lattice relaxation time T_1 with the decay rate of the energy fluctuations in the spin system. A formal expression for this decay rate can be obtained from an extension of the damping-constant formalism developed by Mori and Kawasaki.[18] If $\mathcal{E}_{\vec{k}}$ denotes the spatial Fourier transform of the energy-density operator for the magnetic system exclusive of the spin-phonon coupling, then the decay rate $\Gamma_{\vec{k}}$ of the relaxation function $(\mathcal{E}_{\vec{k}}(t), \mathcal{E}_{\vec{k}}^{\dagger})$ can be written

$$\Gamma_{\vec{k}} = (1/2kT)\int_{-\infty}^{\infty} dt \langle\{\dot{\mathcal{E}}_{\vec{k}}(t),\ \dot{\mathcal{E}}_{\vec{k}}^{\dagger}\}\rangle (\mathcal{E}_{\vec{k}},\ \mathcal{E}_{\vec{k}}^{\dagger})^{-1} \ . \quad (1)$$

Here $\dot{A} = (i/\hbar)[\mathcal{H}, A]$, where $\mathcal{H}$ is the total Hamiltonian of the coupled systems, the dagger denotes adjoint, k is Boltzmann's constant, and the curly brackets imply a symmetrized product. The function $(\mathcal{E}_{\vec{k}},\ \mathcal{E}_{\vec{k}}^{\dagger})$ is given by

$$(\mathcal{E}_{\vec{k}},\ \mathcal{E}_{\vec{k}}^{\dagger}) = \int_0^{\beta} d\lambda \langle e^{\lambda}\mathcal{E}_{\vec{k}} e^{-\lambda}\mathcal{E}_{\vec{k}}^{\dagger}\rangle - \beta\langle\mathcal{E}_{\vec{k}}\rangle\langle\mathcal{E}_{\vec{k}}^{\dagger}\rangle \ , \quad (2)$$

where $\beta = (kT)^{-1}$ and the angular brackets indicate an ensemble average over the coupled systems.

In order to separate the effects of diffusion from those associated with spin-lattice relaxation, we pass to the $k = 0$ limit of (1) in which case $\mathcal{E}_0$ is equal to $\mathcal{H}_s$, the Hamiltonian of the spin systems, and Γ_0 is equal to $1/T_1$. If the Hamiltonian of the coupled systems is written

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_p + \mathcal{H}_{\rm int} \ , \quad (3)$$

where $\mathcal{H}_p$ is the phonon part and $\mathcal{H}_{\rm int}$ is the spin-phonon coupling, then Eq. (1) reduces to

$$\Gamma_0 = 1/T_1 = (1/2\hbar^2)\int_{-\infty}^{\infty} dt \times \langle\{[\mathcal{H}_s,\ \mathcal{H}_{\rm int}](t),\ [\mathcal{H}_s,\ \mathcal{H}_{\rm int}]^{\dagger}\}\rangle (kT^2C_H)^{-1} \ , \quad (4)$$

where C_H, the magnetic specific heat, is given by

$$C_H = (\mathcal{E}_0,\ \mathcal{E}_0)/T \ . \quad (5)$$

In the spirit of perturbation theory we can replace the Hamiltonian $\mathcal{H}$, which is implicit in Eq. (4), by $\mathcal{H}_s + \mathcal{H}_p$, the Hamiltonian of the uncoupled spin and phonon systems. If we denote the eigenvalues of $\mathcal{H}_s$ by E_m and E_n and those of $\mathcal{H}_p$ by E_μ and E_ν, then Eq. (4) reduces to

$$1/T_1 = \sum_{m,n} (E_m - E_n)^2 e^{-\beta E_m} W_{mn} \Big/ 2kT^2C_H \sum_m e^{-\beta E_m} \ , \quad (6)$$

where W_{mn}, the transition rate from m to n, is given by

$$W_{mn} = Z_p^{-1}\sum_{\mu,\nu} e^{-\beta E_\mu}(2\pi/\hbar)\left|\langle m\mu\left|\mathcal{H}_{\rm int}\right|\nu n\rangle\right|^2 \times \delta(E_m + E_\mu - E_n - E_\nu) \ , \quad (7)$$

in which Z_p denotes the partition function for the phonons.

Two comments are appropriate here. First, T_1 is proportional to C_H, as is anticipated in the thermodynamic arguments of Casimir and du Pré.[19] Because of this, the relaxation time increases as the critical point is approached and, in principle, becomes infinite at T_c. Second, if we pass to the high-temperature limit, we recover the familiar Hebel-Slichter formula[20]

$$1/T_1 = \sum_{m,n} (E_m - E_n)^2 W_{mn} \Big/ 2\sum_m E_m^2 \ . \quad (8)$$

Up to now we have made no mention of the detailed structure of $\mathcal{H}_{\rm int}$. Henceforth, we will assume that

the interaction is linear in the atomic displacements. This assumption, together with the first-order perturbation approximation implicit in Eq. (6), restricts our analysis to one-phonon processes. This is an important restriction. In dilute salts, multiphonon processes become the dominant relaxation mechanism whenever $kT \gg \bar{E}$, where $\bar{E}$ is a measure of the typical separation between thermally populated levels of the paramagnetic ion. We can estimate $\bar{E}$ for the concentrated systems from the mean-square internal field $\langle H_I^2 \rangle$. For a system with an exchange interaction $-2J\vec{S}_1 \cdot \vec{S}_2$ between nearest neighbors we find[21]

$$\bar{E} \simeq g\mu_B \langle H_I^2 \rangle^{1/2} = [2zS(S+1)]^{1/2} J \ , \tag{9}$$

where z is the number of nearest neighbors. If we use the molecular-field expression for the critical temperature,

$$kT_c = \tfrac{2}{3} zJS(S+1) \ , \tag{10}$$

we have

$$\bar{E} \simeq 3kT_c / [2zS(S+1)]^{1/2} \ . \tag{11}$$

Thus, for T near T_c, $\bar{E}$ is roughly comparable to kT. As a consequence, we expect that near the critical point the dominant relaxation processes will involve only one phonon. For $T \gg T_c$, multiphonon processes will probably be important.

At this point it is convenient to consider separately two limiting cases. In the first of these, $\bar{E}$ (or kT_c) is assumed to be larger than, or comparable to, the energy associated with the peak in the density of states of the acoustic-phonon modes. If this happens, then all the acoustic modes are "on speaking terms" with the spin system. As a consequence the relaxation can take place very quickly. The second case pertains to the opposite limit. If $\bar{E}$ is much smaller than the peak energy, only a small fraction of the acoustic modes can interact with the spin system in a one-phonon process. The relaxation then takes place slowly.

In anticipation of the discussion in Sec. III we consider as an example of rapid relaxation a system where the dominant coupling comes from the strain dependence of the exchange interaction. In this case $\mathcal{H}_{\rm int}$ can be written

$$\mathcal{H}_{\rm int} = \sum_{i,j} \frac{\partial J_{ij}}{\partial \vec{r}_{ij}} \cdot (\vec{U}_i - \vec{U}_j)\vec{S}_i \cdot \vec{S}_j \ , \tag{12}$$

where $\vec{U}_i$ denotes the displacement of the ith magnetic ion from its equilibrium position, J_{ij} is the exchange integral, and $\vec{S}$ is the spin. The $\vec{U}_i$ can be expanded in the normal coordinates of the phonons:

$$\vec{U}_i = (-i) \sum_{\vec{k},p} \left(\frac{h}{2m\omega_{\vec{k},p} N} \right)^{1/2} \times \vec{\epsilon}(\vec{k}, p)(a^\dagger_{\vec{k},p} - a_{-\vec{k},p}) e^{i\vec{k}\cdot\vec{r}_i} \ , \tag{13}$$

where $\vec{\epsilon}(\vec{k}, p)$ is the polarization and $\omega_{\vec{k},p}$ the frequency of the mode designated by $\vec{k}, p$, with which are associated annihilation and creation operators $a_{\vec{k},p}$ and $a^\dagger_{\vec{k},p}$. Also, m is the mass of the magnetic ion, $\vec{r}_i$ denotes the position of the ith unit cell, and N is the number of unit cells.

The calculation of the relaxation time which follows from Eq. (12) is straightforward. If we assume an exchange interaction between nearest neighbors which depends only on the distance between them, we find that T_1 can be written

$$\frac{1}{T_1} = \frac{W_M^2}{2kT_c^2 C_H} \left(\frac{\partial \ln J}{\partial \ln r} \right)^2 \left(\frac{\hbar^2 k T_c}{m W_M^2 r^2} \right) \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt\, e^{-iW_M t/\hbar} \times \langle\langle \{J_k(t), J_k^\dagger\} \rangle\rangle_{\rm av} \ , \tag{14}$$

where

$$J_{\vec{k}} = J \sum_i e^{i\vec{k}\cdot\vec{r}_i} \sum_j{}' (1 - e^{i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)}) \vec{S}_i \cdot \vec{S}_j \tag{15}$$

with the sum over j being restricted to the z nearest neighbors of the site i which are located a distance r away. The double bracket $\langle\langle \cdots \rangle\rangle$ indicates a second average over the Brillouin zone of the phonons. In obtaining (14) we have neglected the contribution from the optical modes and have approximated the spectrum of acoustic modes by an Einstein oscillator with frequency $W_M/\hbar$. We identify W_M with the energy of the peak in the phonon density of states.

The relaxation time is seen to depend on four factors: (i) a dimensionless thermodynamic factor $W_M^2/kT_c^2 C_H$; (ii) a dimensionless coupling constant $\partial \ln J / \partial \ln r$; (iii) $(\hbar^2 kT_c / m W_M^2 r^2)$, the ratio of mean-square displacement to (nearest-neighbor distance)^2; (iv) and finally the Fourier transform of the correlation of the fluctuations of the operator $J_{\vec{k}}$ average over the surface of the Brillouin zone. Of these four, the last is the most important.

In discussing this function it is convenient to write it in the form

$$\langle\langle \{J_{\vec{k}}(t), J_{\vec{k}}^\dagger\} \rangle\rangle_{\rm av} = \langle\langle J_{\vec{k}} J_{-\vec{k}} \rangle\rangle_{\rm av} R(t) \ , \tag{16}$$

where

$$R(t) = \langle\langle \{J_{\vec{k}}(t), J_{\vec{k}}^\dagger\} \rangle\rangle_{\rm av} (\langle\langle J_{\vec{k}} J_{-\vec{k}} \rangle\rangle_{\rm av})^{-1} \ . \tag{17}$$

The function $\langle\langle J_{\vec{k}} J_{-\vec{k}} \rangle\rangle_{\rm av}$, which involves the equal-time short-wavelength fluctuations of an operator similar to the energy density, we believe to be adequately approximated by its value calculated in the high-temperature limit where all spin states are equally populated. Thermal averages taken in this limit are denoted by $\langle \cdots \rangle_0$. We approximate $R(t)$ by a Gaussian $\exp(-\Delta^2 t^2)$ whose width Δ^{-1} is equal to $\hbar / g\mu_B \langle H_I^2 \rangle^{1/2}$. The justification for such an approximation will be discussed later. At the moment, we only say that it amounts to assuming that the power spectrum of $J_{\vec{k}}$ for $\vec{k}$ on the zone boundary has appreciable weight out to frequencies

on the order of the precession frequency in the root-mean-square internal field. With these approximations we obtain the expression

$$\frac{1}{T_1}=\frac{W_M^2}{2kT^2C_H}\left(\frac{\partial \ln J}{\partial \ln r}\right)^2\frac{\hbar^2 kT_c}{mW_M^2 r^2}\langle\langle J_{\vec{k}}J_{-\vec{k}}\rangle\rangle_0\frac{\sqrt{\pi}}{\hbar g\mu_B}$$
$$\times\langle H_I^2\rangle^{1/2}\exp[-W_M^2/4g^2\mu_B^2\langle H_I^2\rangle],\quad kT_c\gtrsim W_M. \tag{18}$$

The calculation of the relaxation time in the limit $kT_c \ll W_M$ is similar to the calculation of the field-dependent relaxation time in dilute salts.[22,23] We employ the average strain approximation[16] in which $\mathcal{H}_{\rm int}$ is written

$$\mathcal{H}_{\rm int}=\sum_i\sum_{\vec{k},p}\left(\frac{\hbar}{2Mvk}\right)^{1/2}(a_{\vec{k}p}^{\dagger}+a_{-\vec{k}p})\,e^{i\vec{k}\cdot\vec{r}_i}f_i. \tag{19}$$

Here M is the mass of the crystal, v is the velocity of sound, and f_i denotes a combination of spin operators appropriate to the ith site. Concommitant with this approximation is the use of a Debye spectrum for the phonons where $\omega_{\vec{k},p}=vk$.

At this point, it is necessary to distinguish between the cases where $\sum_i f_i$ commutes with $\mathcal{H}_s$ and the cases where it does not. If $\sum_i f_i$ does not commute with $\mathcal{H}_s$, as in the case of the orbit-lattice interaction, then the relaxation time can be written

$$\frac{1}{T_1}=\left(\frac{1}{2kT_c^2C_H}\right)\frac{3kT_c\sum_{m,n}(E_m-E_n)^4|\langle n|\sum_i f_i|m\rangle|^2}{2\pi\rho v^5\hbar^4\sum_m(1)},$$
$$kT_c\ll W_M \tag{20}$$

where ρ is the mass density. Apart from the average strain model, the only approximation we have made in obtaining Eq. (20) is to evaluate the correlation function of $[\mathcal{H}_s, \mathcal{H}_{\rm int}]$ in the high-temperature long-wavelength limit. Since we do not expect $\sum_i f_i$ to show critical behavior, such an approximation is suitable for order-of-magnitude estimates.

The relaxation time given by Eq. (20) is seen to involve the fourth moment of $\sum_i f_i$. Were $\sum_i f_i$ to commute with $\mathcal{H}_s$, the fourth moment would vanish identically. Such is the case when f_i is proportional to the energy density e_i. When this happens, it is necessary to retain the factor $\exp(i\vec{k}\cdot\vec{r}_i)$ in the sum over i in (19). In detail, if the coupling is through the energy density, we have

$$f_i=\frac{\partial \ln J}{\partial \epsilon}\,e_i. \tag{21}$$

The relaxation time that results can be written

$$\frac{1}{T_1}=\left(\frac{1}{2kT_c^2C_H}\right)\frac{A_6^E kT_c}{2\pi\rho v_t^7\hbar^6}\left(\frac{\partial \ln J}{\partial \epsilon}\right)^2,\quad kT_c\ll W_M. \tag{22}$$

Here A_6^E denotes the coefficient of k^2 in the sixth moment of the temporal Fourier transform of the energy-density correlation function

$$\langle \mathcal{E}_{\vec{k}}(t)\mathcal{E}_{\vec{k}}^{\dagger}\rangle_0=\frac{\mathrm{Tr}(\sum_i e^{i\vec{k}\cdot\vec{r}_i}e_i(t)\sum_i e^{-i\vec{k}\cdot\vec{r}_i}e_i)}{\mathrm{Tr}1}, \tag{23}$$

in which the symbol Tr denotes trace, and

$$\mathcal{E}_{\vec{k}}=\sum_i e^{i\vec{k}\cdot\vec{r}_i}e_i.$$

The dependence of T_1 on the longitudinal sound velocity v_l is a consequence of the assumption that the exchange interaction depends only on the distance between neighboring spins.

As indicated in Eq. (23), we have anticipated that the sixth moment of the energy-density correlation function can be satisfactorily approximated by its high-temperature limit. An argument justifying this approximation can be developed along the lines of the argument for the slow variation of the thermal conductivity.[10] We will not go into detail here except to state that an analysis similar to that in Ref. 10 indicates that the major contribution to the moments of the energy-density correlation function comes from wave vectors $\vec{q}$ which exceed the inverse of the correlation length. For this reason we do not expect any anomalous behavior when the correlation length becomes very large, as long as there is only a mild increase in the specific heat over its value away from the critical region.

Equations (18), (20), and (22) are the principal results of this section. We discuss their application in Sec. III.

III. APPLICATIONS

In this section we consider in sequence spin-lattice relaxation in $RbMnF_3$, MnF_2, and EuO. The first step in such an analysis is to determine the dominant spin-phonon coupling. Information on this matter can be obtained from a comparison of the attenuation of the longitudinal and shear waves. In all three systems it is found that the strongest coupling for phonons with frequencies on the order of 100 MHz is through the strain dependence of the exchange integral (volume magnetostriction).[24] We suppose this is the case for thermal phonons as well. As a consequence, we expect that the relaxation time will be given by either Eq. (18) or Eq. (22).

In the case of $RbMnF_3$, optical studies of phonon sidebands indicate that the first peak in the phonon density of states is found in the vicinity of 76 cm^{-1} (104 °K).[25,26] Since the Néel temperature for the system is 83 °K, it appears that $RbMnF_3$ comes close to being in the category $kT_c\gtrsim W_M$, where Eq. (18) is applicable. In this equation, the calculation of $\langle\langle J_{\vec{k}}J_{-\vec{k}}\rangle\rangle_0$ is straightforward. The magnetic lattice is simple cubic with dominant nearest-neighbor interactions. We have

$$\langle J_{\vec{k}}J_{-\vec{k}}\rangle_0=\tfrac{4}{3}[S(S+1)]^2J^2$$
$$\times(\sin^2 k_x a+\sin^2 k_y a+\sin^2 k_z a). \tag{24}$$

Since the Brillouin zones for the magnetic and crystal lattices are the same, we find

$$\langle\langle J_{\vec{k}}\, J_{-\vec{k}}\rangle\rangle_0 = \tfrac{4}{3}[S(S+1)]^2 J^2 N$$

$$= \tfrac{1}{3} k T^2 C_H^* , \qquad (25)$$

where C_H^* is the high-temperature approximation to the magnetic specific heat:

$$C_H^* = \frac{2}{3}\,\frac{z[S(S+1)]^2 J^2}{kT^2} N . \qquad (26)$$

With the values $J = 3.4\ ^\circ\mathrm{K}$, [27] $S = \frac{5}{2}$ and $z = 6$, $g\mu_B \langle H_I^2\rangle^{1/2}$ is equal to $35\ ^\circ\mathrm{K}$. We estimate $\partial \ln J/\partial \ln r \approx -10$, which is what one would expect if $RbMnF_3$ followed the "$\frac{10}{3}$" law for the volume derivative of the Néel temperature. [28] With $r = 4.2$ Å and $m = 0.92 \times 10^{-22}$ g, we obtain the result

$$1/T_1 = 5\times 10^{10}(C_H^*/C_H)\ \mathrm{sec}^{-1} . \qquad (27)$$

For $|1 - T_N/T| = 10^{-2}$, $C_H^*/C_H = 0.3$, [29] so that $T_1 = 0.7\times 10^{-10}$ sec. This estimate is in qualitative agreement with the value $T_1 = 3\times 10^{-10}$ sec reported in Ref. 13.

Optical studies of sidebands in MnF_2, where $T_N = 67\ ^\circ\mathrm{K}$ suggest a peak in the phonon density of states in the vicinity of $100\ \mathrm{cm}^{-1}$ ($136\ ^\circ\mathrm{K}$). [30] Consequently, this system falls somewhere between our two limits. With this in mind, we can still obtain a crude estimate for T_1 from (18). With $g\mu_B \langle H_I^2\rangle^{1/2} = 21\ ^\circ\mathrm{K}$ we obtain the result

$$1/T_1 \approx 10^7 (C_H^*/C_H)\ \mathrm{sec}^{-1} , \qquad (28)$$

which is at least a factor of 30 longer than the relaxation time inferred by Kawasaki and Ikushima. [7] Since $W_M^2/4g^2\mu_B^2\langle H_I^2\rangle$ [the argument of the exponential in Eq. (18)] $\simeq 10.5$ for this system, the analysis is particularly sensitive to the approximation used for the high-frequency tail of the power spectrum of $J_{\vec{k}}(t)$. As a consequence, we do not believe the discrepancy between the two values of T_1 is particularly significant.

The behavior of EuO is somewhat puzzling. According to the interpretation given in Ref. 9, the decay of the energy fluctuations whose wave vectors are commensurate with the phonon wave vector is dominated by diffusion. If this is the case, the spin-lattice relaxation time, the energy-diffusion constant (D_E), and the acoustic frequency ω must obey the inequality

$$1/T_1 < D_E(\omega/v)^2 < \omega , \qquad (29)$$

where v is the sound velocity.

A reasonable estimate of D_E is provided by the high-temperature limit of the spin-diffusion constant D_S. We estimate the latter from the moments of the normalized spin-correlation function [18]:

$$(C_H/C_H^*) D_E \approx D_S(\infty) \simeq (\pi/2)^{1/2}\,\frac{\langle\omega_k^2\rangle_S^{3/2}}{k^2\langle\omega_k^4\rangle_S^{1/2}} . \qquad (30)$$

Using expression for the second and fourth moments given by Collins and Marshall [31] we obtain the result

$$(C_H/C_H^*) D_E \simeq 0.5(Ja^2/\hbar)\,[S(S+1)]^{1/2}, \qquad (31)$$

for the fcc EuO lattice.

Thus with $a = 5.1$ Å, $J = 0.8\ ^\circ\mathrm{K}$, [32] and $S = \frac{7}{2}$ we have

$$(C_H/C_H^*) D_E \approx 10^{-3}\ \mathrm{cm}^2\,\mathrm{sec}^{-1}. \qquad (32)$$

In the experiments reported in Ref. 9 the frequency ranged from 50 to 170 MHz. With $v = 5\times 10^5$ cm sec^{-1}, the inequality $D_E(\omega/v)^2 < \omega$ was always satisfied. If $1/T_1$ is less than $D_E(\omega/v)^2$ for $\omega/2\pi = 50$ MHz, then $T_1(C_H^*/C_H)$ must be greater than 10^{-3}–10^{-4} sec. As we will see, this is about 2 orders of magnitude longer than the time we estimate.

We have been unable to determine the positions of the peaks in the phonon density of states in EuO. However, the long relaxation times needed to explain the ultrasonic data suggest that this system is in the category $kT_c \ll W_M$, in which case Eq. (22) is applicable.

In order to obtain an estimate of A_0^E we make the following argument. We define a normalized correlation function $S(t)$ by

$$\langle \mathcal{E}_{\vec{k}}(t)\, \mathcal{E}_{\vec{k}}^{\dagger}\rangle_0 = \langle \mathcal{E}_{\vec{k}} \mathcal{E}_{-\vec{k}}\rangle_0 S(t) . \qquad (33)$$

The quantity A_0^E can be written as the product of $\langle \mathcal{E}_0 \mathcal{E}_0\rangle_0$ with the quadratic term in the sixth moment of the Fourier transform of $S(t)$. Since the calculation of the sixth moment of the energy-density correlation function is prohibitively complex, we approximate it by the sixth moment of the Fourier transform of the normalized spin-correlation function $\langle S_{\vec{k}}^z(t) S_{\vec{k}}^{z\dagger}\rangle_0 / \langle S_{\vec{k}}^z S_{-\vec{k}}^z\rangle_0$. Justification for such an approximation comes from a comparison of the second and fourth moments of the spin- and energy-density correlation functions of a Heisenberg chain with nearest-neighbor interactions. For small k and $S \gg 1$, we find [31,33]

$$\langle\omega_k^2\rangle_E / \langle\omega_k^2\rangle_S = 1, \qquad (34)$$

$$\langle\omega_k^4\rangle_E / \langle\omega_k^4\rangle_S = \tfrac{1}{2}, \qquad (35)$$

where S and E refer to the spin and energy functions, respectively.

Recent studies of the sixth moment of the spin-correlation function indicate that

$$\langle\omega_k^6\rangle_S \approx 4\,\langle\omega_k^2\rangle_S\,(\langle\omega_k^4\rangle_S / \langle\omega_k^2\rangle_S)^2 \qquad (36)$$

for small k. [34] Using formulas given in Ref. 31 we estimate A_6^E for the EuO lattice:

$$A_6^E = 3.7\times 10^4 [S(S+1)]^3 J^6 a^2 \langle \mathcal{E}_0 \mathcal{E}_0\rangle_0 , \qquad (37)$$

where a is the lattice parameter.

For $\partial \ln J/\partial \ln \epsilon$, we take the value 5.3 reported by Argyle *et al.* [35] Thus with $v_l = 5\times 10^5$ cm sec^{-1}, [36] $T_c = 77\ ^\circ\mathrm{K}$, $\rho = 8$ g cm^{-3}, [37] and the values given previously for J and a, we obtain the result

$$1/T_1 = 2.5\times 10^5\,(C_H^*/C_H)\ \mathrm{sec}^{-1}, \qquad (38)$$

which is to be compared with the value 10^3–10^4 (C_H^*/C_H) sec^{-1} inferred by postulating diffusive decay. We postpone discussion of the significance of this difference until Sec. IV.

IV. DISCUSSION

The calculated values for the relaxation time in $RbMnF_3$ and, to a lesser extent, MnF_2 are in rather good agreement with the values inferred from ultrasonic data. We believe this supports the interpretation that the attenuation is dominated by the dynamics of the energy fluctuations. In the case of EuO the agreement is not as good. The relaxation time of 10^{-3} – 10^{-4} sec, which follows from our estimate of the energy-diffusion constant, is about a hundred times longer than the time we calculate.

Because of this discrepancy, we are led to consider an alternative explanation for the absence of the divergence.[13,38] This explanation follows from the observation the that attenuation would be nonsingular if the decay of the energy fluctuations were governed by the spin-lattice mechanism, provided $\omega T_1 \gg 1$. This condition is satisfied for our values of T_1 for the frequencies employed in the experiment. We note, also, that if there is no divergence and energy diffusion is more important than spin-lattice relaxation, then the attenuation is predicted to be proportional to ω^2, whereas if spin-lattice effects were dominant, the attenuation is independent of frequency. However, because of background problems, it is not possible to establish the frequency dependence of that part of the attenuation associated with the coupling to the energy density.[38]

A major source of error may be the calculation of T_1 itself. The most suspect approximation involves the estimate of A_6^E. Although we do not expect the correlation function for the energy-density fluctuations to vary much from its high-temperature limit as long as $C_H^*/C_H \gtrsim 0.1$, even a mild change can have a pronounced effect on the sixth moment. Unfortunately we have no way of estimating the magnitude of such an effect. It may also be the case that the relaxation near T_c is dominated by multiphonon processes. In his measurement of the relaxation time of Eu^{++} in CaF_2, Huang[39] obtained a value for T_1 which extrapolates to 10^{-6} sec at $T = 77\,^\circ$K.

In the light of all these factors, it is our opinion that the question of the relaxation time (and the attenuation) in EuO can only be resolved by a direct measurement of T_1.

Finally, we would like to comment briefly on the approximation for $\langle\langle\{J_{\vec{k}}(t),\ J_{\vec{k}}^\dagger\}\rangle\rangle_{av}$ and also on the question of the divergence of the thermal conductivity in antiferromagnets. As pointed out in Sec. II, we write $\langle\langle\{J_{\vec{k}}(t),\ J_{\vec{k}}^\dagger\}\rangle\rangle_{av}$ as the product of $\langle\langle J_{\vec{k}} J_{-\vec{k}}\rangle\rangle_{av}$ and the normalized function $R(t)$. We approximate $R(t)$ by a Gaussian whose width is determined by the precession frequency in the root-mean-square internal field. As we will see, such an approximation appears to be satisfactory in the high-temperature limit. Since the wave vectors of interest are on the zone boundary, whereas the critical energy fluctuations involve wave vectors near the center of the zone, we argue that it is satisfactory near T_c as well.

Information on the behavior of $R(t)$ in the high-temperature limit can be obtained from an analysis of the moments of its Fourier transform. In order to avoid the algebraic complications arising from the factor $1 - \exp[i\vec{k}\cdot(\vec{r}_i - \vec{r}_j)]$, we will consider instead the dynamically similar normalized energy-density correlation function $\langle\mathcal{E}_{\vec{k}}(t)\,\mathcal{E}_{\vec{k}}^\dagger\rangle_0/\langle\mathcal{E}_{\vec{k}}\mathcal{E}_{-\vec{k}}\rangle_0$. The second moment of the Fourier transform of this correlation function in a simple cubic lattice can be written in the form[40]

$$\begin{aligned}\langle\omega_{\vec{k}}^2\rangle_E = \tfrac{2}{3}S(S+1)(2J)^2\,(15 &- \cos 2k_x a - \cos 2k_y a \\ &- \cos 2k_z a - 4\cos k_x a\cos k_y a - 4\cos k_x a\cos k_z a \\ &- 4\cos k_y a\cos k_z a)\,(1 + \tfrac{1}{3}\cos k_x a + \tfrac{1}{3}\cos k_y a \\ &+ \tfrac{1}{3}\cos k_z a)^{-1}\,. \end{aligned} \tag{39}$$

An estimate of the breadth of the power spectrum of $J_{\vec{k}}$ can be obtained by averaging the numerator and denominator of $\langle\omega_k^2\rangle_E$ over the surface of the zone. We find

$$\begin{aligned}\langle\langle\omega_k^2\rangle_E\rangle &= \tfrac{56}{3}\,S(S+1)J^2\,, \\ &= 1.6 g^2\,\mu_B^2\langle H_I^2\rangle\,, \end{aligned} \tag{40}$$

which we interpret as supporting our approximation for $R(t)$.

Our final point concerns the possibility of a divergence in the thermal conductivity of an antiferromagnet in the region above the Néel point. Although there is theoretical evidence that the conductivity remains finite as $T \to T_N+$,[11] recent measurements of the frequency-dependent longitudinal staggered susceptibility in MnF_2 *below* T_N have been interpreted as indicating that the thermal conductivity diverges as $(T_N - T)^{-0.28}$ when $T \to T_N-$.[41] The question then arises as to whether there is a similar divergence above T_N which could account for the weak divergence in the attenuation in $RbMnF_3$ and MnF_2. We argue against this.

Our argument against the thermal-conductivity interpretation rests on the magnitude of the decay rates for the energy fluctuations. If the thermal conductivity were symmetric about T_N, then we would expect that at a temperature $T_N + \Delta T$, D_E would be approximately equal to D_E at $T_N - \Delta T$. According to Ref. 41 for $T_N - T = 0.02\,^\circ$K, $D_E \approx 3.6 \times 10^{-3}$ cm^2 sec^{-1}. For ultrasonic frequencies on the order of 100 MHz and sound velocities of 5×10^5, the decay rates of the energy fluctuations would be

on the order of 6×10^3 sec^{-1} which is 5 to 6 orders of magnitude smaller than the decay rates inferred from the ultrasonic data for both $RbMnF_3$ and MnF_2.

Note added in proof. Measurement of the parameter $\partial \ln J/\partial \ln r$ for $RbMnF_3$ were reported by B. Golding, J. Appl. Phys. (to be published). He obtained the value -9.4 ± 0.9 which is within experimental error of our estimate -10.

ACKNOWLEDGMENT

The author would like to thank Professor B. Lüthi for many helpful discussions and communications.

†Research supported by the National Science Foundation.

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

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

[3]B. Lüthi and R. J. Pollina, Phys. Rev. 167, 488 (1968).

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

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

[6]G. E. Laramore and L. P. Kadanoff, Phys. Rev. 187, 619 (1969).

[7]K. Kawasaki and A. Ikushima, Phys. Rev. B 1, 3143 (1970).

[8]R. J. Pollina and B. Lüthi, Phys. Rev. 177, 841 (1969).

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

[10]D. L. Huber, Solid State Commun. 6, 685 (1968).

[11]K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 40, 706 (1968).

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

[13]G. Gorodetsky, B. Lüthi, and T. J. Moran, Intern. J. Magn. (to be published).

[14]Our interpretation of the data reported in Ref. 7 goes somewhat beyond the interpretation given by the authors in that we identify their τ with the spin-lattice relaxation time. In view of our estimates for the relaxation time in MnF_2 this identification does not seem unreasonable, although other mechanisms cannot be ruled out.

[15]J. H. Van Vleck, Phys. Rev. 57, 426 (1940).

[16]R. Orbach, Proc. Roy. Soc. (London) A264, 458 (1961).

[17]M. Blume and R. Orbach, Phys. Rev. 127, 1587 (1962).

[18]H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 27, 529 (1963).

[19]H. B. G. Casimir and F. K. du Pré, Physica 5, 507 (1938).

[20]L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959).

[21]We define our mean-square internal field in such a way that at high temperatures the specific heat can be written as the specific heat of an assembly of noninteracting spins in a field $\langle H_I^2\rangle^{1/2}$.

[22]R. Orbach, Proc. Roy. Soc. (London) A264, 485 (1961).

[23]D. Huber, Phys. Rev. 131, 190 (1963).

[24]B. Lüthi, P. Papon, and R. J. Pollina, J. Appl. Phys. 40, 1029 (1969).

[25]M. W. Passow, thesis, University of Wisconsin, 1969 (unpublished).

[26]C. H. Perry and E. F. Young, J. Appl. Phys. 38, 4624 (1967).

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

[28]D. Bloch, J. Phys. Chem. Solids 27, 881 (1966).

[29]D. T. Teaney, V. L. Moruzzi, and B. E. Argyle, J. Appl. Phys. 37, 1122 (1966).

[30]D. D. Sell, R. L. Greene, and R. M. White, Phys. Rev. 158, 489 (1967). Our estimate of W_M comes from Fig. 2 of this paper. It is based on the separation between the phonon structure at 18 520 cm^{-1} and the $E1$ line at 18 418 cm^{-1}.

[31]M. F. Collins and W. Marshall, Proc. Phys. Soc. (London) 92, 390 (1967).

[32]T. R. McGuire, B. F. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. 34, 1345 (1963).

[33]D. L. Huber, J. Semura, and C. G. Windsor, Phys. Rev. 186, 534 (1969).

[34]D. L. Huber, Phys. Letters 31A, 267 (1970).

[35]B. E. Argyle, N. Miyata, and T. D. Schultz, Phys. Rev. 160, 413 (1967).

[36]Estimated from values for the elastic constants reported in Ref. 35.

[37]C. F. Guerci and M. W. Shafer, J. Appl. Phys. 37, 1406 (1966).

[38]B. Lüthi (private communication).

[39]C. Y. Huang, Phys. Rev. A139, 241 (1965).

[40]A. G. Redfield and W. N. Yu, Phys. Rev. 169, 443 (1968).

[41]M. P. Schulhof, P. Heller, R. Nathans, and A. Linz, Phys. Rev. Letters 24, 1184 (1970).