Critical Attenuation of Sound in Gadolinium*

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We present ultrasonic attenuation measurements in the vicinity of the Curie temperature. Longitudinal waves along the c axis exhibit a large critical attenuation, whereas transverse waves show only a spurious attenuation peak. Along the a axis, the critical attenuation for longitudinal waves is much smaller. In a nonsymmetry direction, both longitudinal and transverse waves show large critical attenuation. All these results can be explained by assuming that the spin-phonon coupling is of the volume magnetostrictive type. For longitudinal waves propagating along either the c or the a axis, we find the following attenuation law for the frequency range 30–180 Mc/sec and $(T-T_c)/T_c>1\times10^{-3}$: $\alpha\propto\omega^2(T-T_c)^{-1.2\pm0.1}$. For temperatures nearer to T_c, the attenuation remains finite. Theories of this effect can account quantitatively for the frequency dependence but not for the temperature dependence.

INTRODUCTION

THE study of transport properties at magnetic phase transitions is receiving much attention recently. In particular, ultrasonic attenuation at magnetic phase transitions was investigated theoretically by several groups.[1–5] However, there exist so far only a few qualitative experimental results in antiferromagnets[6–8] (MnF_2, Cr, and MnTe). We present here quantitative results of ultrasonic attenuation in ferromagnetic gadolinium. The critical attenuation arises because the large spin fluctuations give rise to an increasing scattering cross section for the sound waves as T approaches T_c.

In the next section we discuss the experiment. We then present experimental results which enable us to determine the spin-phonon coupling mechanism responsible for critical scattering. Finally, we give quantitative results for the paramagnetic region and discuss these in the light of these recent theories.

EXPERIMENT

From an ingot of gadolinium single crystal, grown by R. J. Gambino of the IBM Watson Research Center, we machined with a spark cutter three single crystals of cylindrical shape, approximately 6 mm in length and 3 mm in diameter. The crystallographic directions of the cylinder axes were the hexagonal c axis, the a axis in the hexagonal plane, and a direction 53° off the c axis.

Little is known about the impurity content of the crystals. But we noticed that the Curie temperatures of these three single crystals varied slightly, although they were cut from the same ingot: T_c (c-cut crystal) = 290.4°K, T_c (a-cut) = 290.2°K, T_c (53° off c axis) = 290.4°K. Finally the ratio of the electrical resistivity at 300 and 4.2°K was measured to be 50 for one of these crystals.

The experiments were carried out in the frequency range 30–180 Mc/sec, using standard pulse-echo techniques. The pulse-height differences of the echoes were measured using a calibrated attenuator. We typically started with 10 to 20 multiple reflections at high temperature and were left with 1 or 2 at T_c for the lower frequencies.

The temperature was controlled using a water bath and a heater with feedback control. The temperature stability was better than 0.01°C. The temperature gradient across the sample, measured with a differential copper-constantan thermocouple, was always less than 0.01°C.

RESULTS AND DISCUSSION

A. Coupling Mechanism

We first show some experimental results which enable us to determine the spin-phonon coupling mechanism.[9] Figure 1 shows the longitudinal and transverse sound attenuation for propagation along the hexagonal c axis for a frequency $\nu=50$ Mc/sec. The longitudinal wave exhibits a total change in attenuation of 31 dB/cm as one moves from high temperatures through T_c. The corresponding change for shear waves is about 0.6 dB/cm. We can think of two spin-phonon coupling mechanisms: (1) the magnetostrictive coupling (also called single-ion or spin-orbit type magnetostriction), which is linear in the strain and quadratic in the spin components; and (2) the volume magnetostrictive coupling (two-ion or forced magnetostriction) which arises from the modulation of the exchange interaction by the strain field. We shall see later from the frequency dependence of the critical attenuation that we can neglect possible higher-order coupling mechanisms.

* Work supported by the National Science Foundation and the Rutgers Research Council.
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The results shown in Fig. 1 enable us to select one of these two mechanisms. The magnetostriction constants for Gd have been measured[10]: For $T=0°K$, $(-\lambda_A+4\lambda_D-\lambda_C)=120\times10^{-6}$ and $\lambda_C=88\times10^{-6}$. ($\lambda$=magnetostriction constants.) The first of these gives the shear magnetoelastic coupling constant $B_{44}=50\times10^6$ erg/cc (using $\rho=7.9$ g/cc and for the sound velocity $C_+=1.64\times10^5$ cm/sec). The second does not give the longitudinal B_{33} directly, but only part of it, as 70×10^6 erg/cc. However, since all magnetostriction constants are of the same order, we can conclude that B_{44} and B_{33} are of the same order of magnitude. Therefore, the linear magnetoelastic coupling mechanism is unable to explain the big difference in attenuation shown in Fig. 1.

One can estimate the volume magnetostrictive coupling either from the pressure dependence of the Curie temperature T_c or from forced magnetostriction results, the former being the more reliable one. One gets[11] $\partial \ln T_c/\partial \ln V=2.0$. With $J(q=0)=36°K$ [12] and $N=3\times10^{22}$ per cc, we get for the coupling constant $B_V=NR\partial J/\partial R\simeq400\times10^6$ erg/cc almost an order of magnitude bigger than the single-ion coupling constants. As we shall see below, the volume magnetostrictive mechanism does not give any contribution to the critical attenuation of transverse waves along the c axis. In the cross section for sound waves, the coupling constant enters quadratically. Therefore, the square of the ratio of the two-ion to the single-ion coupling, about 100, is sufficient to rule out the single-ion mechanism. The slight anomaly for the transverse sound attenuation in Fig. 1 can be partly attributed to such a single-ion mechanism and partly to a small misalignment (2°) of the crystal.

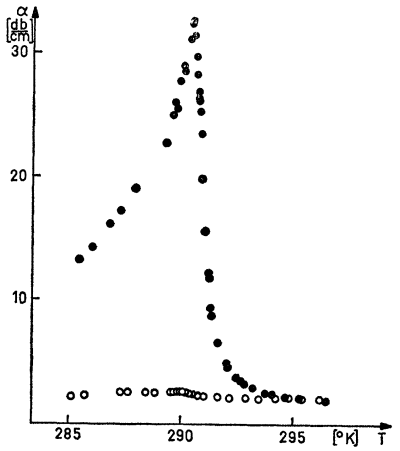

FIG. 1. Critical attenuation of sound in Gd. Propagation along c axis, $\nu=50$ Mc/sec. ●, longitudinal; ○, transverse.

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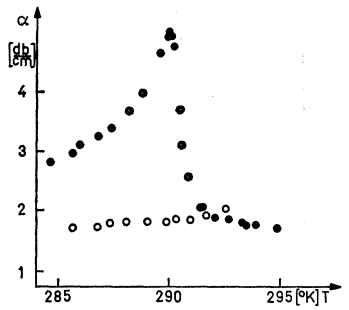

FIG. 2. Critical attenuation of sound in Gd. Propagation along a axis, $\nu=50$ Mc/sec. ●, longitudinal; ○, transverse, polarization vector e in hexagonal plane.

For a sound wave with wave vector $\mathbf{q}$, polarization vector $\mathbf{e}_q$, amplitude A, and lattice vector $\mathbf{R}$, the volume magnetostrictive interaction in the long-wavelength approximation reads

$$\mathcal{H}'=\sum_{i,\mathbf{R}}\frac{\partial J}{\partial \mathbf{R}}\cdot(\mathbf{u}_{i+\mathbf{R}}-\mathbf{u}_i)\mathbf{S}_i\cdot\mathbf{S}_{i+\mathbf{R}}$$

$$=\sum_{i,\mathbf{R}}A\left(\frac{\partial J}{\partial \mathbf{R}}\cdot\mathbf{e}_q\right)(\mathbf{R}\cdot\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{R}_i)(\mathbf{S}_i\cdot\mathbf{S}_{i+\mathbf{R}}). \quad (1)$$

It follows from (1) that there is no coupling of transverse sound waves propagating along symmetry directions, assuming $\partial J/\partial \mathbf{R}$ to be a vector with components $(\partial J/\partial a, \partial J/\partial a, \partial J/\partial c)$.

Figure 2 shows the case of a sound wave propagating along the a axis in the hexagonal plane. Again, the longitudinal sound wave exhibits critical scattering, but reduced considerably compared to the c-axis case from 31 to 3.4 dB/cm. This is in nice agreement with analogous observations in anomalous thermal expansion[13] and volume magnetostriction[14] experiments, where one also observes an order of magnitude larger effect in the c direction compared to the a direction. It means that the quantity $a(\partial J/\partial a)$ is an order of magnitude smaller than $c(\partial J/\partial c)$. Again, transverse sound waves do not couple in this geometry in accordance with Eq. (1). Linear magnetoelastic coupling constants are again of the same order of magnitude, both for longitudinal and shear waves, and not responsible for critical scattering.

Finally, Fig. 3 shows attenuation results for propagation in a nonsymmetry direction. The propagation direction is 53° off the c axis. Here both the quasi-longitudinal and quasitransverse waves exhibit large critical attenuation in accordance with the volume magnetostrictive mechanism explained above. The subsidiary peaks in the transverse wave attenuation in the ferromagnetic region are probably due to domain wall effects.

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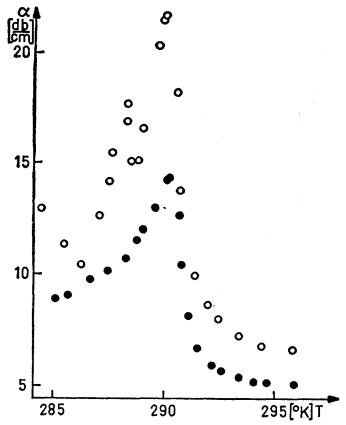

FIG. 3. Critical attenuation of sound in Gd. Propagation direction 53° off the c axis, $\nu=50$ Mc/sec. ●, longitudinal; ○, transverse.

Preliminary experiments on sound attenuation at the Néel point $T_N=179$°K in dysprosium show critical attenuation both for longitudinal and shear waves, propagating along the c direction. In dysprosium, the linear magnetoelastic coupling constants are an order of magnitude larger[15] than the ones for gadolinium, since the Dy^{3+} ion is a non-S-state ion. Hence the linear magnetoelastic mechanism is at least comparable in strength to the volume magnetostrictive mechanism.

B. Sound Attenuation in the Paramagnetic Region

We focus our attention now on sound-wave attenuation in the paramagnetic region, which is the most favorable region for a quantitative comparison between experiment and theory.

Figure 4 shows a double logarithmic plot of attenuation (background attenuation subtracted) versus the temperature difference $\Delta T=T-T_c$. This is for the case of longitudinal sound waves of various frequencies with propagation along the c axis. The background attenuation was estimated for $\Delta T>20$°C. Analogous measurements in dysprosium, which has similar elastic properties, did not show any noticeable temperature dependence of this background attenuation in the temperature region 280–320°K. It shows an approximately linear frequency dependence. It affects the experimental values of the anomalous attenuation critically only for frequencies lower than 30 Mc/sec.

Figure 4 shows that one has an inverse power law for the critical attenuation for $\Delta T>1$°C: $\alpha\propto(T-T_c)^{-\eta}$ with $\eta=1.2\pm0.1$. The error limit gives the largest deviations of the exponent η for the frequency range 30–180 Mc/sec. The exponent η for the individual frequencies is listed in the figure caption to Fig. 4. There is a small but noticeable trend of η from higher values at lower frequencies to smaller values at higher frequencies. It should be noted that along the a axis longitudinal sound waves exhibit an inverse power law with the same exponent for $\Delta T>1$°C.

As seen from Fig. 4 and also from Figs. 1–3, the attenuation remains finite for $\Delta T<1$°C. This effect occurs in the region outside the applicability of the theories to be discussed below. We believe that it is due to impurities, which also have a big effect on T_c as noted above. Therefore it is premature to investigate this region quantitatively. *Note added in proof.* Further measurements in the temperature region $T-T_c<0.8$°C revealed the following attenuation law: $\alpha\propto\omega^{3/2}e^{-\gamma(T-T_c)^2}$ with $\gamma=2.2$°C^{-2}. This Gaussian law may be further evidence that the attenuation in this temperature region is controlled by impurities.

The frequency dependence of the critical attenuation for $\Delta T>1$°C is displayed in Fig. 5 in a double logarithmic plot. At all temperatures ΔT from 1.5 to 15°C an ω^2 law is closely observed, the variation of the exponent being 1.8 to 2.1. The spin-phonon Hamiltonians discussed above give an interaction term linear in the sound-wave wave vector $\mathbf{q}$, which for the scattering cross section and the attenuation leads to an ω^2 dependence. This is further evidence that it is not necessary to consider coupling mechanisms which are of higher order in the phonon amplitudes. The theories[3] discussed below show the ω^2 law to be rigorously valid.

Preliminary measurements did not show any change in the sound velocity in the critical region up to an accuracy of 2%, which is to be expected from the theories discussed below.[3]

C. Comparison with Theory

With the interaction Hamiltonian (1) one can calculate the sound attenuation, by calculating the rate of creation of phonons minus the rate of destruction of phonons with wave vector $\mathbf{q}$. Instead of expressing the result in terms of the matrix elements of the eigenstates of the spin system, one usually uses the correlation

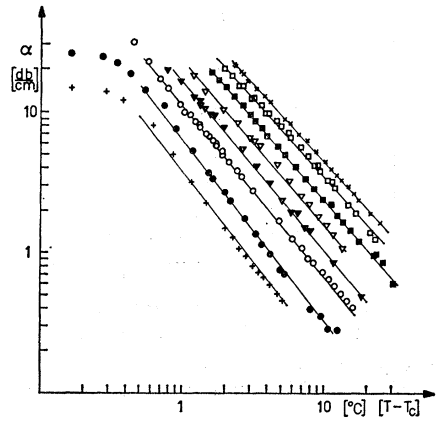

FIG. 4. Temperature dependence of ultrasound in Gd. +, 36 Mc/sec ($\eta=1.29$); ●, 50 (1.27); ○, 70 (1.20); ▼, 90 (1.16); ▽, 108 (1.17); ■, 130 (1.16); □, 150 (1.12); ×, 180 (1.12).

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function description. Thus the attenuation coefficient α reads[16]

$$\alpha=\frac{\pi}{cM\omega}\sum_{RR'}\left(\mathbf{R}^{-1}\frac{\partial J}{\partial \mathbf{R}}\right)^2(\mathbf{R}\cdot\mathbf{e}_q)(\mathbf{R}'\cdot\mathbf{e}_q)(\mathbf{R}\cdot\mathbf{q})(\mathbf{R}'\cdot\mathbf{q})$$
$$\times[1-\exp(\hbar\omega/kT)](2\pi\hbar)^{-1}\sum_{i,j}\int_{-\infty}^{\infty}\langle Q_iQ_j(t)\rangle$$
$$\times\exp[i\mathbf{q}(\mathbf{R}_i-\mathbf{R}_j)]\exp(i\omega t)\,dt, \quad (2)$$

where $Q_i=\mathbf{S}_i\cdot\mathbf{S}_{i+R}$ and $Q_i(t)$ is the Heisenberg representation of the operator Q_i. $\langle\cdots\rangle$ denotes statistical average. The term in front of the integral (the first sum) we have already dealt with in the discussion of the coupling mechanism. It determines essentially the directional and polarization dependence of the attenuation. The sum over i, j of the integral we denote by $S(q, \omega)$, the Fourier transform of the space-time four-spin correlation function. The crucial point in the theory of ultrasonic attenuation is to evaluate this $S(q, \omega)$.

As already mentioned, there are several papers dealing with the theory of ultrasonic attenuation.[1–5] They differ mainly in the treatment of the four-spin correlations. All these theories employ a factorization procedure in breaking the four-spin correlations into pair correlations. Since the fluctuations become large near T_c, this factorization procedure must become invalid close to T_c. In Table I the results of these theories are listed together with our experimental result. Papoular[1] considers an interaction Hamiltonian, which is quadratic both in the spin and the phonon variables. He therefore does not get an ω^2 dependence. Bennett and Pytte express their result in terms of the static susceptibility χ and the spin diffusion constant D, by relating the spin pair correlation function to the spectral weight function. For the volume magnetostrictive interaction they get $\alpha\propto\omega^2\chi^{3/2}/D$. This gives for the exponent $\eta=1.6$–2.5. The lower limit 1.6 stems from taking D constant and[17] $\chi\propto(T-T_c)^{-1.1}$.

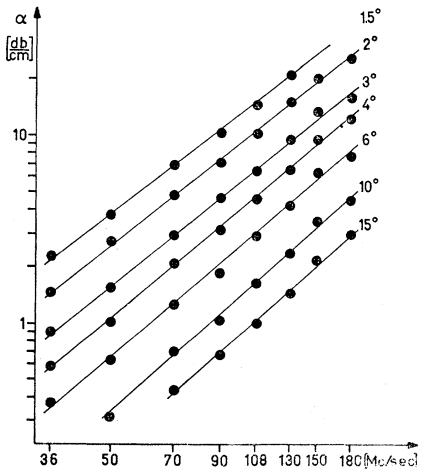

FIG. 5. Frequency dependence of ultrasound in Gd. The temperatures of the isotherms are indicated ($\Delta T=1.5$ to 15°C).

TABLE I. Frequency and temperature dependence of ultrasonic attenuation in the paramagnetic region. Comparison of theory with experiment.

Authors	Attenuation law
Papoular[a]	$\omega^3(T-T_c)^{-0.5}$
Tani and Mori[b]	$\omega^2(T-T_c)^{-1}$
Bennett and Pytte[c]	$\omega^2(T-T_c)^{-1.6\text{ to }-2.5}$
Kashcheev[d]	$\omega^2(T-T_c)^{-5.4}$
Okamoto[e]	$\omega^2(T-T_c)^{-2.5}$
Experiment	$\omega^2(T-T_c)^{-1.2\pm0.1}$

[a] See Ref. 1.
[b] See Ref. 2.
[c] See Ref. 3.
[d] See Ref. 4.
[e] See Ref. 5.

Our experimental results do not agree closely with either of these theoretical results. In fact our experimentally determined exponent η lies between the ones calculated by Tani and Mori[2] and Bennett and Pytte.[3]

On the other hand, the frequency dependence agrees with the theories, with the exception mentioned above. Bennett and Pytte[3] show that the ω^2 law is not affected by the factorization procedure of the four-spin correlations, but that it is rigorously valid.

D. Concluding Remarks

Several points should be emphasized in conjunction with these results:

(1) Gadolinium, showing a long-range indirect exchange,[12] is not a typical Heisenberg ferromagnet. However, the theories discussed above are not restricted to nearest-neighbor exchange. Therefore they should also be applicable to gadolinium.

(2) The theories discussed above are strictly valid only for cubic materials. No serious consequences should result since the experimentally determined critical attenuation obeys the same temperature dependence for propagation along the c and a axis as mentioned above.

(3) The factorization of the four-spin correlation function, common to all these theories, overestimates the critical fluctuations and therefore leads to too large a value of the exponent η as shown by the most reliable theories.[3,5] This was noted by Bennett and Pytte[3] by calculating in the same approximation the specific heat, which turned out too singular. Theoretical estimates[3,18] show that correlations of three and four spins become important for temperatures $T-T_c/T_c<10^{-2}$, which for Gd results in $\Delta T\leq3$°C. However, our results suggest that they become important already for $\Delta T\leq20$°C.

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(4) There have been theories developed[16,19] for the phonon thermal conductivity at magnetic phase transitions employing the coupling term (1). Since they also use the small-q approximation, these theories are in principle equivalent to the theory of ultrasonic attenuation. They, however, do not use the factorization procedure. They can express their result in terms of the specific heat C and the spin thermal conductivity κ. In this way the sound attenuation, or the reciprocal of the phonon relaxation time, becomes proportional to κ, all other singular factors cancelling. A theory for κ at the magnetic phase transition has not been developed so far. Similar ideas have recently been expressed by Huber.[20]

ACKNOWLEDGMENTS

Further experiments, studying other magnetic substances, are in progress. Informative discussions with Dr. Abrahams, Dr. Bennett, Dr. Huber, and Dr. Pytte are gratefully acknowledged.

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Spin-Lattice Interaction in UO_2. II. Theory of the First-Order Phase Transition

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A theory of the first-order phase transition in UO_2 is presented and discussed in the molecular-field approximation. An isotropic nearest-neighbor exchange and local quadrupole-lattice interaction are taken as the basic interactions in the model. Interesting behavior is obtained due to the two distinct ways in which the collective ground-state degeneracy can be removed at $T=0°K$: a cooperative Jahn-Teller distortion or a polarization of the sublattice magnetization by the exchange field. Depending on the relative gain in free energy obtained by these two mechanisms, one obtains four different types of behavior near the critical point: (1) a second-order transition to a distorted state with no magnetic ordering; (2) a second-order transition to a distorted state followed by a second-order magnetic transition; (3) a first-order transition yielding a discontinuous change in lattice distortion and sublattice magnetization; (4) a second-order magnetic transition accompanied by a weak distortion. The temperature dependence of the elastic constant C_{44} is also derived. The parameters required to give a first-order transition in agreement with the measured discontinuity in sublattice magnetization and the correct behavior for C_{44} are found to be consistent with the parameters obtained from the measured spin-wave excitations.

I. INTRODUCTION

INTERACTION between the single-ion ground state and lattice is expected to be large in systems where the ground-state degeneracy is associated with the orbital state of the electrons. In a concentrated system both the collective ground state and low-lying electronic excitations will be significantly modified by this interaction. Uranium dioxide is a particularly striking example of this situation. In a previous paper,[1] (henceforth referred to as I), it has been shown that the ground state is characterized by a balance between the exchange and Jahn-Teller (JT) forces and that indirect quadrupole-quadrupole interactions caused by the virtual exchange of an optical phonon must be included to obtain the proper excitation spectra. Since much of the current interest in UO_2 was stimulated by the observations of Frazer *et al.*[2] that the transition to the ordered state was a first-order phase transition and the subsequent explanations of Blume,[3] it is particularly interesting to consider whether the spin-lattice interaction used to obtain the ground state and spin-wave excitations is able to generate the first-order phase transition.

In the following, the thermodynamic properties of UO_2 are derived in the molecular-field approximation. Interesting effects are obtained due to the two distinct ways in which the ground state degeneracy can be removed at $T=0°K$—a cooperative JT distortion or the usual polarization of the sublattice magnetization

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