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Microwave phonon attenuation in rare-earth garnets: Ion-phonon interactions

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Significant deviations from the behavior usual for dielectrics are observed in the ultrasonic attenuation at gigahertz frequencies in Nd, Gd, and Tb garnets and are attributed to the rare-earth ions. Relaxation of low-lying electron states by Orbach processes satisfactorily explains attenuation peaks in neodymium gallium garnet and terbium scandium aluminum garnet near 60 K. Below 20 K the attenuation in all these garnets, irrespective of electronic structure, increases as the inverse of temperature and the square of frequency. Mechanisms that could explain these results based on the relaxation of low-lying states are proposed. The lack of knowledge about the parameters entering the theoretical models prevents a detailed comparison with experiment at this time.

I. INTRODUCTION

This paper discusses ultrasonic attenuation at gigahertz frequencies in several rare-earth aluminum and gallium garnets between 1.5 and 300 K. Significant deviations from the behavior usually observed in dielectric crystals, where most of the loss arises from phonon-phonon interactions, were noted in the attenuation in Nd, Gd, and Tb garnets and appear to be due to the rare-earth ions. Previous measurements of thermal conductivity showed similar effects.[1]

The crystals used in this study and some of their physical properties are listed in Table I. Nd^{3+}, Gd^{3+}, and Tb^{3+} ions in the garnet lattice all have electronic energy levels within 120 cm^{-1} of the ground state which arise from the crystal-field splitting of the lowest multiplet of the free ion[4–7] (Fig. 1). Only the levels below 120 cm^{-1} are shown. Except for Tb^{3+}, these ions exhibit Kramers's degenerate electron states which must belong to the single two-dimensional irreducible representation of the double group D_2. All levels of Tb^{3+} are nondegenerate.

The use of scandium-substituted garnets was dictated by availability of crystals and was not expected to have a large effect on attenuation. Sc^{3+} ions preferentially occupy octahedral sites and ensure that no rare-earth ions enter these positions.[2] They also somewhat enlarge the unit cell, which may reduce the magnitude of the crystal-field effect. For low-lying levels, however, the shift is probably small. Optical-absorption measurements yield a level at 3.4 cm^{-1} and a group of unresolved levels near 80 cm^{-1} in TbScAlG,[4] as compared to 2 cm^{-1}, and 74 and 84 cm^{-1} in TbAlG.[7]

NdGaG and TbAlG undergo magnetic-ordering transitions at 0.51 and 1.35 respectively.[5,6] Unfortunately, our measurements could not be carried to low enough temperatures to ascertain whether or not this ordering influences attenuation.

II. EXPERIMENTAL RESULTS

Samples approximately 5×5×10 mm were cut with their axis parallel to a ⟨100⟩ or ⟨111⟩ direction from boules grown by the Czochralski technique. Thin films of ZnO, dc sputtered onto one end of the samples, constituted efficient and wideband transducers. The pulse-echo technique was used to measure attenuation. Whenever possible, several samples of each composition and orientation were examined with results reproducible to better than ±20%.

A mass-spectrometric analysis[8] was performed on two specimens of GdGaG (Table II). The level

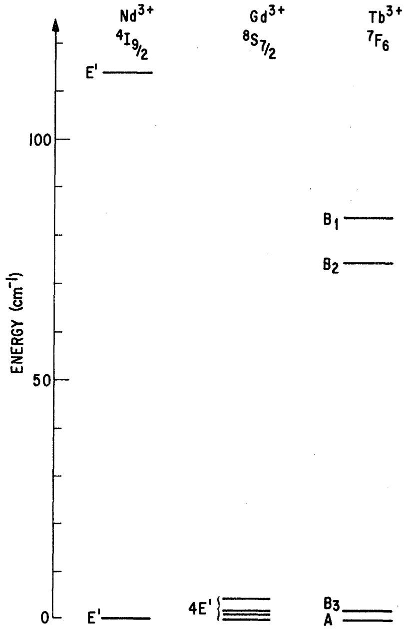

FIG. 1. Lowest energy levels of Nd^{3+}, Gd^{3+}, and Tb^{3+} in NdGaG (Ref. 4), GdGaG (Refs. 5, 6), and TbAlG (Ref. 7), respectively, and their irreducible representations.

TABLE I. Physical properties of garnets.

	Lattice constant (Å)	Longitudinal sound velocity along ⟨111⟩ at 300 K (10^5 cm/sec)	Ultrasonic attenuation along ⟨111⟩ at 2.5 GHz	
			α(300 K) (dB/cm)	α(1.5 K) $-\alpha_0$ (dB/cm)
$Nd_3Ga_5O_{12}$ (NdGaG)	12.509[a]	6.49 ± 0.05	2.3[b]	0.08
$Gd_3Ga_5O_{12}$ (GdGaG)	12.383[c]	6.40 ± 0.05	2.1	0.58
$Gd_3Sc_2Ga_3O_{12}$ (GdScGaG)	12.567[a]	6.45 ± 0.05	2.8	0.64
$Gd_3Sc_2Al_3O_{12}$ (GdScAlG)	13.395[a]	7.09 ± 0.05	2.6	0.28
$Tb_3Sc_2Al_3O_{12}$ (TbScAlG)	12.346[a]	7.1 ± 0.3	5.9[b]	2.40

[a] Reference 2.

[b] In these garnets, there is an electronic contribution to attenuation at room temperature.

[c] Reference 3.

of most transition metal and rare-earth impurities is low. Furthermore, the variability in impurity concentrations between samples is greater than 50%. Since no comparable differences were observed in the attenuation, we conclude that impurities are not responsible for the excess attenuation. The remote possibility that defects present in all crystals with the same concentration are involved cannot be excluded.

At low temperatures, typically below 30 K, the attenuation in dielectric crystals normally levels out at a constant residual attenuation α_0. This is the case in isomorphous yttrium aluminum garnet[9] (YAlG) which contains no paramagnetic ions. In the present garnets, attenuation increases again below 15 K and is nearly proportional to the square of frequency and the inverse of temperature (Figs. 2-5). The minimum attenuation near 15 K, about the same as α_0 in YAlG, was substracted from the data. The magnitude of the excess attenuation depends on orientation and composition (Table I). In the Gd garnets, it is about twice as large along ⟨100⟩ (Fig. 4 and Ref. 10). In the other ones, not enough material was available to make a comparison. The effect of replacing Ga on octahedral sites by Sc is small (Fig. 3), as expected. No change in attenuation at 1.5 K occurred over a 20-dB range of input microwave power.

In TbScAlG, a small reduction in attenuation at 1.5 K was observed in a magnetic field of 1.3 kG transverse to the direction of propagation. This indicates that the excess loss is of electronic origin. In GdGaG and NdGaG, no change could be detected in such a small field.

In two NdGaG and one GdGaG sample oriented along ⟨100⟩, the attenuation was higher than in all others and varied as $\omega T^{-1/2}$.[10] The concentration of dislocations in these crystals was in excess of 50 cm^{-2}, in contrast to a usual 10 cm^{-2} or less. This anomaly was not observed in a sample cut parallel to the growth direction [111] from the

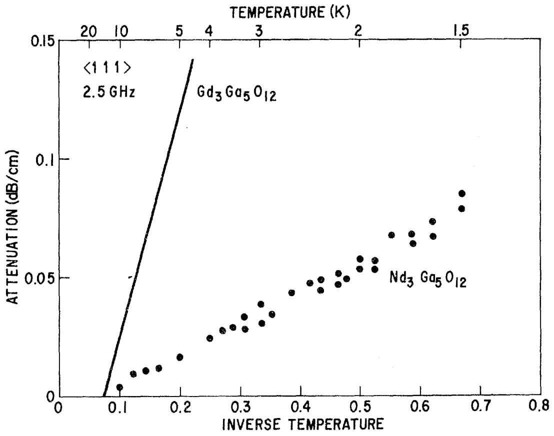

FIG. 2. Low-temperature attenuation in neodymium gallium garnet. The solid line is taken from Fig. 3.

TABLE II. Impurity concentrations in two crystals of GdGaG by mass-spectroscopic analysis (ppm weight). Concentrations of other transition metals and rare earths are less than 0.5 ppm.

Impurity	Sample 1	Sample 2
Ti	1.1	2.2
Cr	0.37	0.51
Fe	20	10
Ni	0.41	0.18
Nb	···	1.6
Mo	···	1.4
Sm	5.3	6.0
Eu	19	80
Tb	1.1	0.18
Dy	< 2.3	1.4
Er	3.0	0.8
Tm	0.75	0.02
Yb	30	1.9

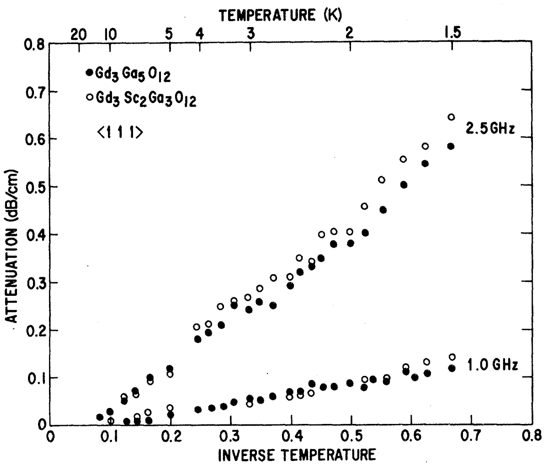

FIG. 3. Low-temperature attenuation in gadolinium gallium garnet.

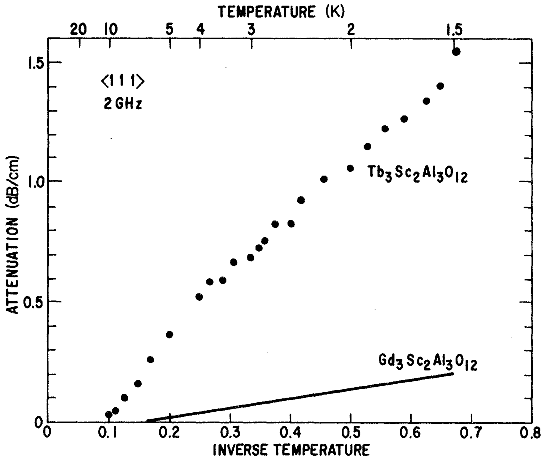

FIG. 5. Low-temperature attenuation in terbium scandium aluminum garnet. The solid line is extrapolated from Fig. 4.

same boule. The absence of the higher attenuation along [111] may be related to the fact that most dislocation lines were parallel to that direction. The influence of dislocations on the attenuation due to bound holes was previously observed in *p*-type silicon.[11]

Above 15 K, attenuation increases rapidly due to phonon-phonon scattering. In Gd garnets this is the only contribution.[9] In NdGaG and TbScAlG, there is an additional peak near 60 K (Figs. 6 and 7). We assume that the electron- and phonon-induced losses are additive and approximate the latter by that measured in GdGaG since attenuation due to phonon-phonon scattering varies little between these garnets.

The excess attenuation shown in Figs. 8 and 9 was normalized to its maximum value. One notes that the peaks are nearly symmetric in $1/T$ and shift without deformation from 1 to 2 GHz. Their positions are almost the same in both garnets. The width of the peak in NdGaG is somewhat less than in TbScAlG. In the latter, a small shoulder is observed on the high-temperature side and may be interpreted as a second peak at about 150 K. The attenuation in NdGaG rises rapidly near room temperature, consistent with a maximum above 300 K.

III. DISCUSSION

The present experimental results indicate that the attenuation in these garnets in excess of that

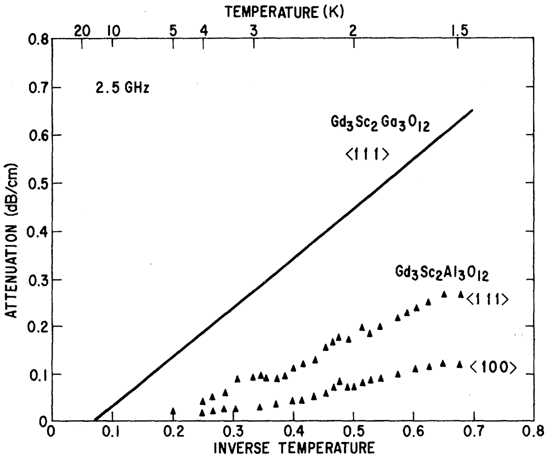

FIG. 4. Low-temperature attenuation in gadolinium scandium aluminum garnet. The solid line is taken from Fig. 3.

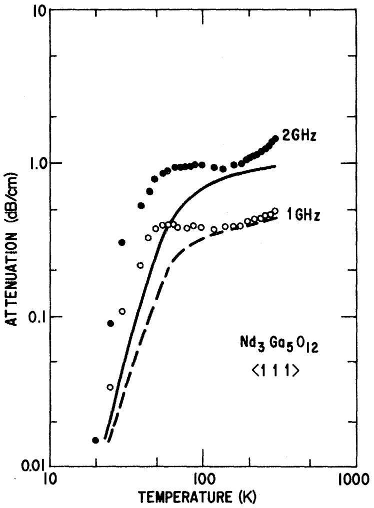

FIG. 6. Attenuation in NdGaG between 20 and 300 K. The curves represent attenuation in GdGaG (Ref. 9).

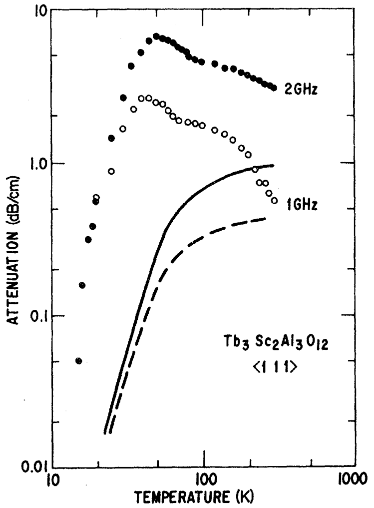

FIG. 7. Attenuation in TbScAlG between 15 and 300 K. The curves represent attenuation in GdGaG (Ref. 9).

normally measured in dielectric crystals is due to rare-earth ions. It is convenient to discuss this phenomenologically in terms of relaxation of the strain-induced perturbation of electron states, which yields an attenuation of the form

$$\alpha = 2\alpha_m \omega^2\tau/(1+\omega^2\tau^2) \quad , \tag{1}$$

where α_m includes the interaction strength and the population factors, τ is a relaxation time, and $\omega = 2\pi f$ (f is the acoustic frequency). In general, both α_m and τ are temperature-dependent. The anisotropy of ion-phonon coupling will affect α_m and can be determined from the symmetry of the electron states.

Garnets crystallize in the cubic space group O_h^{10}, with rare earths normally located on sites of D_2 symmetry. The three orthogonal binary axes attached to each site form a local coordinate system, x, y, and z. There are six possible orientations of these axes relative to the crystal lattice, which define six classes of ions. These classes are equivalent in the absence of strain.

We assume that the coupling of electrons to acoustic waves is linear in the induced strain ϵ and has its symmetry. A time-even operator such as ϵ belonging to an irreducible representation Γ only perturbs the states of an odd-electron ion (e.g., Nd^{3+} and Gd^{3+}) if Γ is contained in the antisymmetric direct product $\{\Gamma_i \times \Gamma_i\}$ of the irreducible representations Γ_i of these states.[12] For even-electron ions (e.g., Tb^{3+}) the symmetric direct product $[\Gamma_i \times \Gamma_i]$ is applicable. Since in D_2, $\{E' \times E'\} = [A \times A] = [B_1 \times B_1] = [B_2 \times B_2] = [B_3 \times B_3] = A$, the energy change due to ϵ can be written

$$\delta U = g_1\epsilon_{xx} + g_2\epsilon_{yy} + g_3\epsilon_{zz} \quad , \tag{2}$$

where ϵ is expressed in the local axes. The coupling constants g_i are related, but not equal, to the usual magnetoelastic constants. We neglect strain-induced mixing of electron states.

To calculate the shift due to a given acoustic mode, one has to decompose the associated strain into the six local-coordinate systems. In general, each class of ions will respond differently. It is straightforward to show that any normal mode will couple to at least one class, so that one will observe attenuation, to a varying extent, for all directions of propagation and polarization.

The temperature and frequency dependence of attenuation in NdGaG and TbScAlG between 15 and 200 K (Figs. 8 and 9) resemble those of a Debye peak obtained from Eq. (1) by assuming that τ follows an Arrhenius law.[13] If we take τ proportional to T^n, corresponding to Raman or direct processes, the agreement is much worse. This strongly suggests that relaxation occurs through Orbach processes involving excited states Nd^{3+} and Tb^{3+}, Δ above the ground state. For this case,[12] $\tau = \tau_0\,(e^{\Delta/kT} - 1)$ and the attenuation is

$$\alpha \propto \frac{1}{T}\,\frac{\omega^2\tau_0\,(e^{\Delta/kT} - 1)}{1 + \omega^2\tau_0^2\,(e^{\Delta/kT} - 1)^2} \tag{3}$$

where α_m has been assumed proportional to $1/T$, as one expects for relaxation of low-lying states.[13] Note that Orbach processes are allowed because of the high Debye temperature Θ of garnets, in contrast to the case of rare-earth-doped ethylsulfates, where $\Theta \approx 60$ K.[14] For Δ, we take the measured separation between the ground state and first excited pair, i.e., 114 cm^{-1} in NdGaG and 82 cm^{-1} for TbScAlG,[4] and τ_0 is adjusted to fit the experi-

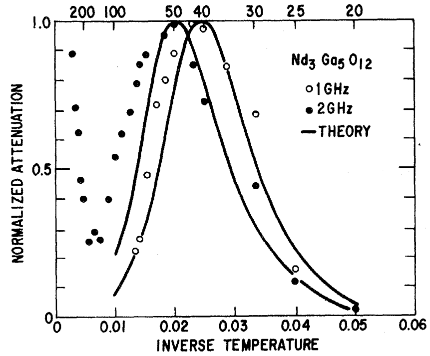

FIG. 8. Normalized excess attenuation in NdGaG at 1 and 2 GHz. Theoretical curves are computed from Eq. (3) with $\Delta/k = 165$ K and $\tau_0 = 4 \times 10^{-12}$ sec.

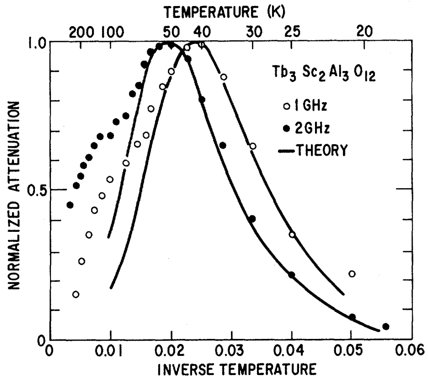

FIG. 9. Normalized excess attenuation in TbScAlG at 1 and 2 GHz. Theoretical curves are computed from Eq. (3) with $\Delta/k = 120$ K and $\tau_0 = 1.4\times10^{-11}$ sec.

mental data. The theoretical curves in Figs. 8 and 9 have been normalized to unity at the maximum. Emphasis was placed on obtaining good agreement below 50 K where errors introduced by the uncertainty about attenuation due to phonon-phonon interactions are small. The deviations above 70 K may be related to the influence of higher states which have been neglected. Also the small splitting of the two lowest pairs of states in TbScAlG has not been taken into account. Nevertheless, the agreement between theory and experiment is quite satisfactory in both cases.

The difficulty with this model lies in identifying the two (or more) low-lying levels between which relaxation occurs. In Tb^{3+}, they could be the A and B_3 levels at 0 and 2 cm^{-1}. Direct transitions between them are slow compared to Orbach processes. However, no such levels are found in Nd^{3+} It is also possible that the hyperfine components of the ground state are involved, a situation realizable in Nd^{3+} and Tb^{3+}. The presence of a similar excess attenuation in TmAlG [15] seems to exclude this possibility. Indeed the nuclear spin of ^{169}Tm is $I = \frac{1}{2}$,[12] and no hyperfine splitting in zero magnetic field is expected in that case. The similarity of the experimental results suggests that the same mechanism applies in all cases.

The interaction is relatively weak. No effect was observed in YAlG and GdGaG doped with about 1-at.% Nd.[9] For comparison, a similar relaxation reported[16] for Cr^{2+} in MgO gave a peak of the magnitude of that in garnets at a concentration of only 20-ppm Cr. This comparative weakness is the result of the isolation of the $4f$ shell from the lattice.

The increase in attenuation at low temperatures is perhaps the most intriguing aspect of our results. It occurs in all four rare-earth garnets in this study, irrespective of the nature of the ground state. Only its magnitude varies (Table I). If this attenuation were related to the lowest crystal-field-split levels between 1 and 5 cm^{-1} (Fig. 1) one would expect a temperature dependence reflecting the variation in the population of these states below 10 K. Optical-absorption spectroscopy in Tb garnets[4] shows that such changes do occur. No process involving these levels has been found to yield the correct dependence on temperature, frequency, and level separation. In general, one would anticipate a maximum in attenuation when $T \approx \Delta/2k$, which, in Tb and Gd garnets is between 1 and 3 K. Clearly this is not observed. Furthermore, in Nd^{3+} no excess attenuation would be predicted, in contradiction with experiment.

Second-order effects such as hyperfine or exchange interactions may be involved. They will further split the energy levels shown in Fig. 1 by small amounts. Relaxation in a system of two or more closely spaced levels can under certain circumstances produce an attenuation increasing as ω^2/T.[17] It is obvious from Eq. (1) that any relaxation process between two levels close enough so that no population changes occur over the contemplated range of temperatures and with a relaxation time nearly independent of temperature and short compared to the period of the acoustic wave, will yield the observed behavior. Also, a distribution of levels can yield an attenuation that approximates a ω^2/T dependence.[18,19] Unfortunately, the lack of knowledge about the parameters that enter the theoretical formalism discourages detailed analysis.

Relaxation *between* ions, rather than within each ion, was discussed in Ref. 10. We showed that if an interaction of the form given in Eq. (2) is assumed, longitudinal waves propagating along $\langle 100\rangle$ or $\langle 111\rangle$ split the rare-earth ions into two groups. Transfer of energy between these groups produces attenuation if it occurs in a finite time τ. This model is quite general and does not rely on any specific relaxation mechanism. In particular, it appears valid for all paramagnetic rare earths. The calculated ratio of attenuation along $\langle 100\rangle$ and $\langle 111\rangle$ of 2.67 compares favorably with a measured value of about 2. However, to account properly for the temperature and frequency dependence of attenuation we need to make two assumptions about τ that are not verifiable at this time, i.e., $\omega\tau \ll 1$ and τ is nearly independent of temperature. These conditions are the same as above. A lower bound on τ can be estimated[20] from the measured change in sound velocity Δs between 1.5 and 20 K. For GdGaG $\Delta s/s \leq 0.3\%$ and $\tau \geq 10^{-13}$ sec. More accurate date for Δs are needed to determine τ as a function of temperature.

IV. SUMMARY

The excess ultrasonic attenuation observed in rare-earth garnets at gigahertz frequencies has been discussed in terms of ion-phonon interactions. The relaxation of low-lying states due to Orbach processes involving excited electron levels satisfactorily describes attenuation peaks near 60 K in NdGaG and TbScAlG. Increases in attenuation below 20 K are not well understood. Two possible mechanisms, absorption due to a weakly split two-level system and relaxation between ions, can account for the experimental behavior under certain circumstances. Additional measurements are needed before their validity can be verified.

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