

Relaxation mechanism of ultrasonic attenuation in Ho-rich $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$

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Temperature-dependent ultrasonic attenuation measurements in the Ho-rich magnetic superconducting system $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ show broad maxima at temperatures around 10 K. A two-energy-level model is proposed and expressions are derived to elucidate the nature of these relaxation-attenuation maxima.

Studies of the interaction between long-range magnetic order and superconductivity of RRh_4B_4 (R : rare earths) in recent years have revealed that crystalline electric fields (CEF's) (Refs. 1 and 2) play an important role in the physical properties of these magnetic superconductors. The CEF removes the degeneracy of the Hund's rule ground state of rare-earth ions in RRh_4B_4 (Refs. 1 and 2) at low temperatures and therefore results in the appearances of Schottky anomalies in specific heat,³ strong magnetic anisotropy,⁴ and deviation of magnetic transition temperature from the trends normally expected.^{2,5} The split of the rare-earth ions's ground states may also affect the propagation of sound waves in these materials.

Temperature-dependent ultrasonic attenuation measurements have been performed on six samples of the $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ system⁶ with $x=1, 0.912, 0.813, 0.6, 0.295,$ and 0 at 15 MHz from 1.5 to 20 K. Except in the regime where the ultrasonic behavior was affected by the onset of the superconducting state, the low-temperature

attenuation data of all the samples but ErRh_4B_4 displayed a broad maximum at temperatures close to 10 K, and the temperature position (T_p) of this maximum depends on the Ho concentration (x) (ErRh_4B_4 has this maximum at 5 K). The same measurements on $\text{Er}_{0.187}\text{Ho}_{0.813}\text{Rh}_4\text{B}_4$ and HoRh_4B_4 at higher sound frequencies show that T_p moves to higher temperatures as the frequency is increased. Such a dependence of T_p on frequency can be the result of an acoustic relaxation process occurring at low temperatures. To find a mechanism for describing this relaxation process, a theoretical model is proposed that considers the effects arising from oscillating the lattice. The derived theoretical results will be compared with the experimental data in this paper.

The temperature-dependent ultrasonic attenuation curves at 15 MHz in zero magnetic field for samples with $x=1, 0.912, 0.813,$ and 0.6 are shown in Fig. 1. The attenuation curves are normalized in the following way: Taking the attenuation at 20 K as the reference of zero

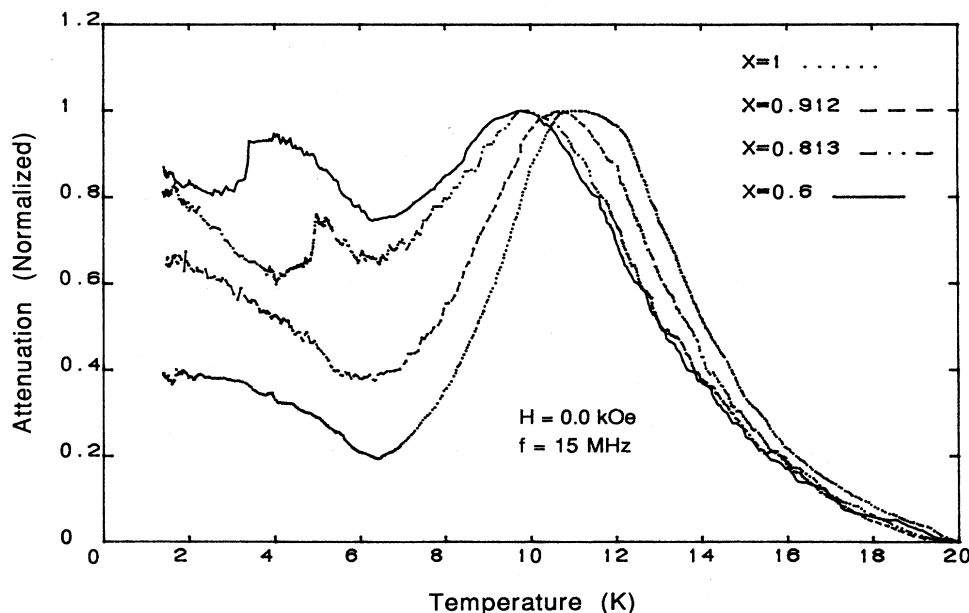


FIG. 1. Temperature-dependent ultrasonic attenuation of $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ with $x=1, 0.912, 0.813,$ and 0.6 at 15 MHz.

attenuation, the attenuation value on each curve at any temperature below 20 K is determined relative to this reference attenuation, and then normalized to the maximum attenuation value of the respective curve. Several features of the attenuation curves can be observed from the figure: (1) The position T_p of the bell-shaped relaxation maximum on each curve shifts to a lower temperature as the concentration x of the Ho atoms decreases. (2) The ratio of the attenuation at the magnetic-phase-transition temperature T_m to the maximum attenuation on each curve increases as x decreases. (3) For the sample with $x=1$, and $x=0.912$, the valleylike relative minimum on the low-temperature side of the bell-shaped maximum of each curve is located at the Curie temperatures of these samples, which are 6.4 K and 6.2 K, respectively. However, for the sample with $x=0.813$ and $x=0.6$, there is a steplike change in attenuation at each Curie temperature, which are 4.95 K and 3.5 K, respectively, and there is a relative minimum at each superconducting phase transition temperature T_{c1} , which are 6.0 K and 6.7 K, respectively. (4) For the reentrant superconductors, the attenuation increases when the temperature is lowered from T_{c1} to T_m . (5) In the ferromagnetic state, the attenuation of all the samples increases as the temperature is lowered.

The bell-shaped attenuation maximum located at temperatures close to 10 K for all the measured samples of the $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ system except ErRh_4B_4 indicates that this maxima is associated with Ho^{3+} ions instead of Er^{3+} ; however, when x is decreased, the effect from Er^{3+} ions becomes stronger, and the temperature-dependent attenuation curve exhibits a second maximum associated with Er^{3+} ions at lower temperatures, such as those shown on the attenuation curves of the sample with $x=0.295$.⁷ In addition, T_p 's of all the bell-shaped maxima stayed unchanged when a constant magnetic field up to 6 kOe was applied.⁶ Experimental results of the other features in the curves shown in Fig. 1 have been analyzed and reported elsewhere,⁶⁻⁸ and because the same mechanism could be applied to the maxima contributed by Ho^{3+} and Er^{3+} individually, let us concentrate the following discussion on feature (1) of the Ho-rich samples.

Figure 2 displays the attenuation as a function of temperature of HoRh_4B_4 at three different frequencies. As is shown, T_p of each curve is 11.1 K, 13.6 K, and 15.2 K for 15 MHz, 50 MHz, and 81.3 MHz, respectively. That is, the temperature position of the bell-shaped maximum is frequency dependent and it moves to higher temperatures as the frequency is increased. The same behavior was also exhibited by $\text{Er}_{0.187}\text{Ho}_{0.813}\text{Rh}_4\text{B}_4$ with T_p 's of 9.9 K and 13 K for 15 MHz and 52.5 MHz, respectively.⁹

Basically, this frequency-dependent behavior can be qualitatively described by a relaxation-attenuation equation,¹⁰

$$\alpha(T)/\alpha_{\max} = 2\omega\tau(T)/[1 + \omega^2\tau^2(T)], \quad (1)$$

where $\alpha(T)$ is the temperature-dependent ultrasonic attenuation; α_{\max} , whose material-dependent parameters will be discussed in detail later, is the maximum of attenuation at angular frequency ω ; and $\tau(T)$ is the temperature-dependent relaxation time which is an in-

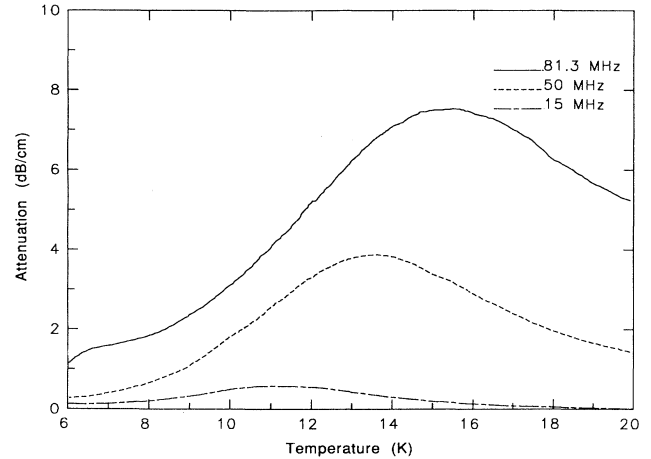


FIG. 2. Temperature-dependent ultrasonic attenuation of HoRh_4B_4 at 15, 50, and 81.3 MHz.

trinsic property of the material. As described in Eq. (1), the temperature at which a relaxation-type attenuation maximum occurs will be determined by the product of ω and τ . Whenever $\omega\tau=1$, α will reach its maximum value at an angular frequency equal to $1/\tau$. However, τ is a temperature-dependent quantity, implying that for one ω , there is one corresponding τ which makes $\omega\tau$ equal to 1, and thereby τ determines the temperature at which $\alpha=\alpha_{\max}$. In fact, we found that τ is a monotonically decreasing function of increasing temperature. Hence, at higher frequencies, α_{\max} is located at higher temperatures.

The energy dissipation of sound waves due to the relaxation process occurring in HoRh_4B_4 can be qualitatively explained as follows. The 17-fold degeneracy of the Hund's rule multiplet of the Ho^{3+} ions is lifted by the CEF's. The strength of the CEF is determined by lattice symmetry, the lattice charge distribution, Steven factors, and radial integrals.¹¹ Therefore, when a stress wave is traveling in the sample, the deformation of the lattice will alter the CEF strength and result in a periodic variation of energy difference between the energy levels. Consequently, the electron populations of each energy will change as well. The lack of instantaneous return of the overpopulated and the underpopulated electron levels to their instantaneous equilibrium states causes the electrons to relax out of phase with respect to the coming stress wave, and results in energy dissipation of the waves.

To quantitatively describe this relaxation attenuation, we begin with a two-level model. Let the energy difference between the two energy levels be ϵ , and let the population densities for the higher-energy level (level 2) and the lower-energy level (level 1) in the equilibrium state be n_{20} and n_{10} , respectively. The transition rates from level 2 to level 1 and from level 1 to level 2 in the equilibrium state will be denoted by k_{21}^0 and k_{12}^0 , respectively. The presence of a sound wave alters the relative numbers of electrons in the two states as well as the transition rates. We denote the number densities and the

transition rates of electrons in the nonequilibrium state for level 1 and level 2 by n_1, k_{12} and n_2, k_{21} , respectively. Then the rate of change of the population in the excited state can be written as

$$dn_2/dt = n_1 k_{12} - n_2 k_{21}. \quad (2)$$

By introducing $\Delta n = n_2 - n_{20}$ and $\Delta k_{12} = k_{12} - k_{12}^0$, and using the Boltzmann relation $n_{20}/n_{10} = \exp(-\varepsilon/k_B T)$, we find that

$$\begin{aligned} \Delta n = & [(n_{20} k_{21}^0 \tau \varepsilon) / (1 + i\omega\tau)] \\ & \times [(\Delta T/T) - (\Delta\varepsilon/\varepsilon)] (1/k_B T), \end{aligned} \quad (3)$$

where $\Delta\varepsilon$ and ΔT represent deviations from their equilibrium values due to the passing of a sound wave, and we have used $(d\Delta n/dt) = i\omega\Delta n$, with ω being the angular frequency of the sound wave. Here τ is defined as $1/(k_{12}^0 + k_{21}^0)$.¹⁰

To simplify our notation, we introduce the quantity

$$C_0 = (n_{20} k_{21}^0 \tau \varepsilon^2 V) / (k_B T^2),$$

which is the Schottky-type heat capacity of a two-level magnetic system at constant volume V and at zero frequency ($\omega=0$), and we define

$$C(\omega) = C_0 / (1 + i\omega\tau).$$

Equation (3) now becomes

$$\varepsilon V \Delta n = C(\omega) T (\Delta T/T - \Delta\varepsilon/\varepsilon). \quad (4)$$

We consider HoRh_4B_4 to be composed of two subsystems; the internal (rare-earth f electrons) subsystem and the external (background thermal phonons) subsystem. The variation of electron occupation number of the magnetic sublattice energy levels causes sound-wave energy loss, and variations of the occupation numbers of the background phonons will also contribute to the dissipation.

For simplicity we adopt Barrett's model¹² for the effect of sound waves on thermal phonons, i.e., we regard the external subsystem of thermal phonons to be lumped into a single effective mode. Let the frequency of this mode be ω_2 , with corresponding energy level $\varepsilon_2 = \hbar\omega_2$, and let Δn_2 be the variation of the phonon occupation number for that mode due to the presence of the sound wave. By extending our analysis for the electron subsystem to the case of the phonon subsystem (see also Ref. 12), we can obtain an expression like Eq. (4). Thus, for each subsystem, we can write

$$\varepsilon_i V \Delta n_i = C_i(\omega) T (\Delta T/T - \Delta\varepsilon_i/\varepsilon_i), \quad (5)$$

where $i=1$ refers to quantities for the electron subsystem and $i=2$ refers to quantities for the phonon subsystem. In particular, for the phonon subsystem

$$C_2(\omega) = C_{20} / (1 + i\omega\tau_2),$$

where C_{20} is the lattice heat capacity (at $\omega=0$) and τ_2 is the phonon relaxation time.

The heat dQ produced in the material as a result of the electron and phonon population variations can be ex-

pressed as¹³

$$dQ = T dS = \sum_{i=1,2} T dS_i, \quad (6)$$

where

$$T dS_i = \varepsilon_i V \Delta n_i = C_i(\omega) T (\Delta T/T - \Delta\varepsilon_i/\varepsilon_i), \quad i=1,2. \quad (7)$$

Introducing the Gruneisen constant

$$\begin{aligned} \Gamma_i &= -\partial \ln(\varepsilon_i) / \partial \ln(V) \\ &= -(V/\varepsilon_i) (\partial \varepsilon_i / \partial V), \end{aligned}$$

we have

$$T dS_i = C_i(\omega) T (\Delta T/T + \Gamma_i \Delta V/V), \quad i=1,2. \quad (8)$$

Since sound-wave propagation is basically an adiabatic process, it follows that $\sum_{i=1,2} T dS_i = 0$, and Eq. (7) then yields

$$\Delta T/T = -(\Delta V/V) [(C_1 \Gamma_1 + C_2 \Gamma_2) / (C_1 + C_2)], \quad (9)$$

where, for notational simplicity, we have written C_i for $C_i(\omega)$. Substitution of expression (9) into Eq. (6) yields

$$\begin{aligned} \varepsilon_i \Delta n_i &= C_i T (\Delta V/V) \\ &\times [\Gamma_i - (C_1 \Gamma_1 + C_2 \Gamma_2) / (C_1 + C_2)]. \end{aligned} \quad (10)$$

The mean energy loss of the sound waves in one oscillation can be expressed as

$$\left\langle \sum_i \Delta n_i (d\varepsilon_i/dt) \right\rangle,$$

which implies that

$$\begin{aligned} \langle dQ/dt \rangle &= -\frac{1}{2} \sum_i \omega \text{Im}(\Delta n_i \Delta \varepsilon_i^*) \\ &= (\omega/2) |\Delta V/V|^2 T (\Gamma_1 - \Gamma_2)^2 \\ &\quad \times \text{Im}[C_1 C_2 / (C_1 + C_2)], \end{aligned} \quad (11)$$

where we have used the relation

$$\Delta \varepsilon_i = -\varepsilon_i \Gamma_i \Delta V/V.$$

Here $\text{Im}(X)$ means the imaginary part of X , and $\Delta \varepsilon_i^*$ is the complex conjugate of $\Delta \varepsilon_i$.

The relationship between the ultrasonic attenuation coefficient α and the energy loss is

$$\alpha = \langle dQ/dt \rangle (\frac{1}{2} |\Delta V/V|^2 \rho v_s^3)^{-1},$$

where ρ is the mass density and v_s is the speed of sound. It follows that

$$\alpha(T) = A \omega T \text{Im}[C_1 C_2 / (C_1 + C_2)], \quad (12)$$

where

$$A = (\Gamma_1 - \Gamma_2)^2 / \rho v_s^3.$$

Explicit evaluation of the factor

$$\text{Im}[C_1 C_2 / (C_1 + C_2)]$$

leads to the final expression

$$\alpha(T) = A (TC_{10}C_{20}/C_t) [\omega^2\tau^*/(1+\omega^2\tau^{*2})], \quad (13)$$

where $C_{i0} = C_i(0)$, and we have defined $C_t = C_{10} + C_{20}$, which is the total heat capacity of the system, and

$$\tau^* = (C_{10}\tau_2 + C_{20}\tau_1)/C_t,$$

which is an effective relaxation time.

Note that $\alpha(T)$ has the characteristic relaxation-attenuation form and that is a function of temperature, sound frequency, and the specific heat as well as the relaxation time of each subsystem.

By using Eq. (13), there are two ways to find the temperature dependence of τ^* from our data. The first is to take the experimental attenuation results of HoRh_4B_4 , and the heat-capacity data of HoRh_4B_4 and LuRh_4B_4 (Ref. 14) to calculate the relaxation time of HoRh_4B_4 at temperatures between 7 and 20 K (at 6.7 K, HoRh_4B_4 underwent a magnetic phase transition). The other approach is to take the ratio of the attenuation at different frequencies. By doing so, the term $f(T)$ ($= AT C_{10} C_{20} / C_t$) will be canceled and τ^* can be determined without employing empirical specific-heat data. Before calculating τ^* by following either of these two ways, we assume that the background attenuation linearly depends on temperature for each frequency, and the attenuation α which arises only from the relaxation process is determined by the expression $\alpha = \alpha_0 - ST + \alpha_c$ (α_0 is the attenuation shown in Fig. 2. S is slope of the straight line for this linear background-attenuation-temperature relationship and is proportional to the frequency of sound wave. T is temperature. α_c is the constant background attenuation whose value does not depend on frequency). Figure 3 shows three curves of the natural logarithm of the τ^* obtained by using three attenuation ratios. These curves are quite close to each other, especially at temperatures below 15 K, which is an indication that Eq. (13) is applicable for interpreting the observed relaxation attenuation. A single function $\tau^*(T)$ can in fact be chosen

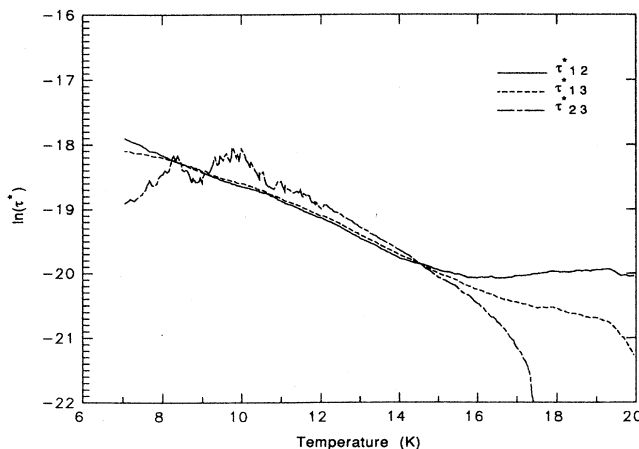


FIG. 3. Relaxation time (τ^*) of HoRh_4B_4 as a function of temperature. τ_{12}^* represents the curve obtained by using the ratio of attenuation at 15 MHz to that at 50 MHz. τ_{23}^* is that for 50 MHz and 81.3 MHz. τ_{13}^* is that for 15 MHz and 81.3 MHz.

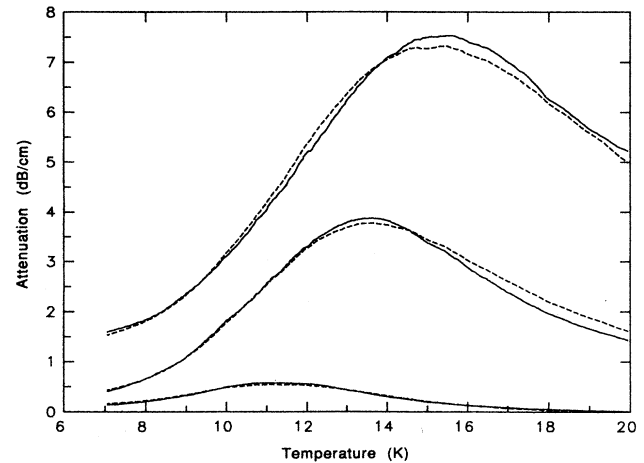


FIG. 4. Comparison of experimental attenuation curves (solid lines) with that of calculated values (dashed lines).

to give a reasonably consistent description of the three measured attenuation curves. The following simple function accomplishes this:

$$\tau^*(T) = 2.27 \times 10^{-8} \exp[-0.26(T-6)]. \quad (14)$$

This function is a rather good straight-line fit to the τ_{13}^* curve in Fig. 3. If the relaxation time of the background phonon subsystem is relatively small or tends to zero, then, $\tau^* \sim C_{20}\tau_1/C_t$ and would be expected to decrease with increasing temperature. Qualitatively, this is consistent with expression (14).

Inserting expression (14) for τ^* into Eq. (13), and using the measured $\alpha(T)$, three sets of functions of $f(T)$ can be calculated. By taking the average of $f(T)$ at each temperature and using expression (14) for τ^* in Eq. (13), we can calculate the ultrasonic attenuation and compare it with the experimental data. The results are shown in Fig. 4. If a 5% experimental error is assumed, the calculated values agree with experimental data quite well. Thus, Fig. 4 shows that the data can be fit with a single τ^* and a single $f(T)$ in the relaxation-attenuation expression (13).

As displayed in Fig. 5, the values of $f(T)$ which are

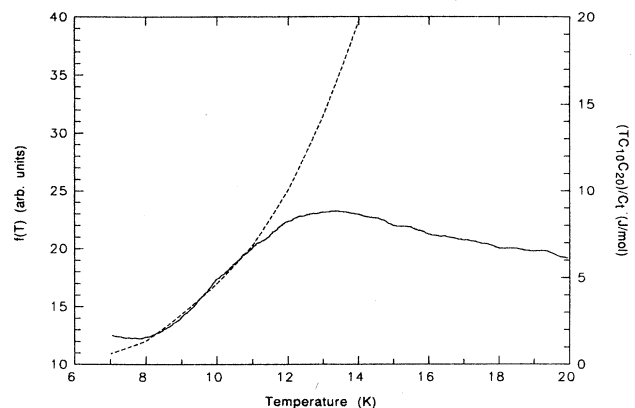


FIG. 5. Comparison of the average of $f(T)$ (solid line) with $TC_{10}C_{20}/C_t$ obtained by employing the experimental data of specific heat (dashed line).

obtained by the procedure stated in the preceding paragraph do not match well with those calculated by using the experimental values of specific heat, C_{10} , C_{20} , and C_1 ,¹⁴ and an appropriately assigned value of A . This disagreement may be attributed to our simplified model. For the Schottky specific heat,

$$C_0 \sim (\epsilon/k_B T)^2 e^{\epsilon/k_B T} / (e^{\epsilon/k_B T} + 1)^2 .$$

If ϵ is 40 K and 60 K (Refs. 1 and 14) which are the energy differences of the first and second excited states from the ground state of Ho^{3+} ions, respectively, and T is between 10 and 20 K, the magnitudes of C_0 from both states will be of the same order, which implies that the 60 K energy level contribution can be a large fraction of C_{10} . Whereas, for attenuation,

$$\alpha \sim C_{10} \tau^* / (1 + \omega^2 \tau^{*2}) ,$$

and τ^* for the higher-energy level is expected to be much smaller than that of the lower-energy level. It follows that the 60 K level would not contribute significantly to α at low temperatures. Thus, while the two-level energy model describes the behavior of relaxation ultrasonic attenuation rather well, the temperature dependence of specific heat involves other excited states with higher values of energy.

We should also mention that a microscopic theory of the influence of CEF effects on ultrasonic attenuation in metallic systems has been given by Becker, Thalmeier, and Flude.¹⁵ These authors obtain an attenuation of the form $\omega^2 F(T)$, where F is a function depending on the details of the CEF-split states. This form is compatible

with the relaxation-attenuation expression (1) in the $\omega\tau \ll 1$ regime, but does not appear to cover the experimental data presented here where $\omega\tau$ varies over a wide range of values. In principle, the theory of Becker *et al.* contains all interactions involving electrons and phonons except for the phonon-phonon interaction. Our model effectively introduces phonon-phonon interaction via a Gruneisen parameter and a relaxation time, and this is a significant difference between our approach and that of Becker *et al.* However, they pay considerable attention to the magnetic field dependence of the magnetoelastic interaction, and therefore such magnetic field data should be analyzed with their model in mind.

In summary, the CEF-split ground states of the magnetic sublattice in $\text{Er}_{1-x}\text{Ho}_x\text{Rh}_4\text{B}_4$ contribute to the relaxation-type ultrasonic attenuation at low temperatures. A theoretical model which considers the oscillating energy levels as a result of the propagation of sound waves in the samples yields a relaxation-type ultrasonic attenuation which is related to the Schottky specific heat. The effective relaxation time which is obtained from our model decreases monotonically with increasing temperature, and this is consistent with the experimental attenuation results.

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