Enhanced Ultrasonic Attenuation in the Superconducting State of Ho-Rich $Er_{1-x}Ho_xRh_4B_4$

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The temperature-dependent and magnetic-field-dependent ultrasonic-attenuation data of Ho-rich $Er_{1-x}Ho_xRh_4B_4$ polycrystalline samples indicate that the attenuation increase observed throughout the superconducting state of this system is associated with the onset and existence of superconductivity. This attenuation behavior is different from any other which has been previously associated with superconductivity, where the attenuation either starts to decrease immediately below T_c or decreases after exhibiting a peak. We suggest that interaction with spin fluctuations or that perhaps a different BCS coherence factor may cause this anomalous behavior.

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Temperature-dependent and magnetic-field-dependent ultrasonic-attenuation measurements on Ho-rich polycrystalline samples of the $Er_{1-x}Ho_xRh_4B_4$ system display anomalous features. The attenuation in the superconducting state of these samples increases as the temperature is lowered from T_{c1} to T_m. There is a sharp change in attenuation at T_m. An applied magnetic field decreases the attenuation in this temperature range as long as the magnitude of the field is below H_{c2}. However, the nonsuperconducting samples in this series exhibit no prominent features at T_m. These data lead us to the following conclusions. The rise in attenuation in the superconducting state is associated with the superconductivity of the sample, since when superconductivity is destroyed either by changing the temperature or by applying a magnetic field the increase in attenuation disappears. This behavior is different from any previously observed in a superconducting system where the sound absorption decreases in the superconducting state. Recently, peaks in attenuation have been observed in the heavy-fermion superconducting systems. However, these peaks either are narrow such as in UBe_{13} or are followed by an eventual decrease in attenuation as in UPt_3 and URu_2Si_2.

Ho and Er are neighbors in the periodic table; the former has eleven f electrons with total angular momentum $J=8$, and the latter has twelve f electrons with $J=\frac{15}{2}$. Both of them have a well localized f-electron shell and the same configuration for the rest of the electrons. However, $HoRh_4B_4$ and $ErRh_4B_4$ have quite different characteristics at low temperatures in spite of their similar crystal structures.[1,2] For example, $HoRh_4B_4$ displays mean-field behavior[3] at its magnetic transition, while $ErRh_4B_4$ shows relatively large spin fluctuations at its Curie temperature T_m.[2] In the $Er_{1-x}Ho_xRh_4B_4$ samples, the Er ions tend to retain the superconductivity caused by the $4d$ electrons in the Rh atoms while the Ho ions tend to destroy it.

Magnetic-susceptibility measurements[4] were the first type of experiments done on the pseudoternary superconductor system $Er_{1-x}Ho_xRh_4B_4$. For $x>0.9$,[5] samples of the $Er_{1-x}Ho_xRh_4B_4$ system exhibit only ferromagnetic transitions. Samples with $x<0.9$ are reentrant superconductors. In the reentrant superconductors, the onset of long-range ferromagnetic order quenches superconductivity at a second critical temperature T_{c2} that is lower than the temperature T_{c1} at which the sample first became superconducting and which is of the order of the Curie temperature.

Specific-heat measurements[6] and zero-field magnetization measurements by neutron diffraction[7] reveal that samples with $x>0.9$ show mean-field behavior. The thermal and magnetic properties of polycrystalline samples of $HoRh_4B_4$ are described well by mean-field theory and are thereby considered to be model ferromagnets with $S=\frac{1}{2}$.[3] However, $ErRh_4B_4$ displays critical spin fluctuations at T_m. Crystalline-electric-field calculations[8] and neutron-diffraction measurements[7,9] show that Ho^{3+} ions in $HoRh_4B_4$ samples order ferromagnetically along the tetragonal c axis;[10] Er^{3+} ions in $ErRh_4B_4$ samples order ferromagnetically in the tetragonal basal plane.[7]

Ultrasonic-attenuation measurements were performed on polycrystalline samples with $x=0$, 0.295, 0.6, 0.813, 0.912, and 1 as a function of temperature and as a function of magnetic field. The samples were synthesized by arc melting the high-purity elements under argon gas, followed by annealing in sealed tantalum tubes at 1200 °C for one week and then at 900 °C for three weeks.[4] They were prepared in the same batches as the samples reported in Ref. 4. It was found that there are many common and self-consistent attenuation characteristics of the $Er_{1-x}Ho_xRh_4B_4$ system. The experimental results of Ho-rich $Er_{1-x}Ho_xRh_4B_4$ will be presented here.

A Matec electromagnetic pulse generator and detector (model 6600) with rf plug in (model 760) was used to produce and detect the sound pulses. The detected pulse train was fed to a Princeton Applied Research boxcar averager (model 162) with plug in (model 165). This system provided sensitivities of better than 0.01 dB. Most of the data were obtained with either a double-echo or single-echo measuring technique. In all cases where both techniques were used, particularly in the sample with $x=0.6$, the measured attenuation curves were the same. Since the first, second, and third echoes exhibited the same behavior, it can be concluded that there was no amplitude dependence. The opposite faces of the samples were parallel to each other and approximately oval in shape. The following table lists the dimensions of the samples in cm; the first two numbers are the major and minor axes of the faces, and the third is the separation between the faces.

Sample	Dimensions (cm)
$x=1$	$1.27\times0.66\times0.87$
$x=0.912$	$0.74\times0.54\times0.43$
$x=0.813$	$0.70\times0.53\times0.43$
$x=0.6$	$0.71\times0.51\times0.45$

A quartz transducer was epoxy bonded to one of the flat faces of each sample. Except for the sample with $x=0.6$ on which both longitudinal and shear wave attenuation were measured, only longitudinal wave attenuation was measured. Both wave modes displayed the same characteristics of attenuation for the sample with $x=0.6$.

The zero-field temperature-dependent ultrasonic-attenuation curves at 15 MHz for the samples with $x=1$, 0.912, 0.813, and 0.6 are shown in Fig. 1. The attenuation curves were normalized in the following way in order to best display the principal features of the data. Taking the attenuation at 20 K as the reference of zero attenuation, the attenuation value on each curve at any temperature below 20 K is determined relative to this reference attenuation, and then divided by the maximum attenuation value of the respective curve. The actual changes in attenuation between 1.5 and 20 K for these curves were $\Delta_a=0.23$ dB/cm, $\Delta_b=0.16$ dB/cm, $\Delta_c=0.14$ dB/cm, and $\Delta_d=0.6$ dB/cm. After the normalization procedure, several features in the attenuation curves become apparent: (1) Close to 10 K, 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 T_m to the maximum attenuation on each curve increases as x decreases. (3) For the samples with $x=1$ and 0.912, the valleylike relative minimum on the low-temperature side of the bell-shaped maximum of each curve is located at T_m, which is 6.4 and 6.2 K, respectively. For the samples with $x=0.813$ and 0.6, there is a steplike change in attenuation at T_m which is 4.95 and 3.45 K, respectively, and there is a relative minimum at each T_{c1}, which is 6 and

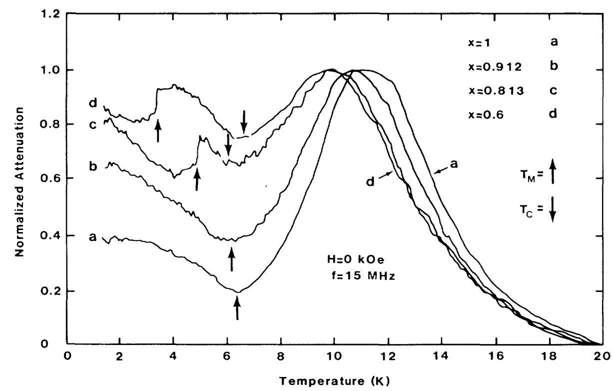

FIG. 1. Temperature dependence of ultrasonic attenuation in samples with $x=1$, 0.912, 0.813, and 0.6 of the $Er_{1-x}Ho_xRh_4B_4$ system. $\alpha(T)$ is normalized (please see text). The magnetic transition, T_m, is indicated by ↑. The superconducting transition, T_c is indicated by ↓. Samples a and b only have magnetic transitions, which occur near the relative minimum in α. Samples c and d have both superconducting transitions, near the relative minimum, and magnetic transitions, at the sharp drop in α. The attenuation increases in the superconducting state of samples c and d. This is the first time such an increase in attenuation has been observed throughout the superconducting state.

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 positions of T_m and T_{c1} in Fig. 1 were determined by ac magnetic-susceptibility measurements which were performed simultaneously with the ultrasonic-attenuation measurements. As may be seen in Fig. 1, the valleylike minima of the samples with $x=1$ and 0.912 are located at the magnetic phase transition temperatures. Since $HoRh_4B_4$ [2] exhibits mean-field behavior in its magnetic, thermal, and transport behavior, the attenuation minimum of $HoRh_4B_4$ at its Curie temperature manifests the fact that the transition has no spin fluctuations. The $Er_{0.088}Ho_{0.912}Rh_4B_4$ sample demonstrates the same fact as well. However, the valleylike attenuation minima of the $Er_{0.4}Ho_{0.6}Rh_4B_4$ and $Er_{0.187}Ho_{0.813}Rh_4B_4$ samples are located at their superconducting transition temperatures T_{c1}, and the steplike changes in attenuation are at the magnetic phase transition temperature T_m. As a matter of fact, the steplike change at T_m is a consequence of the increasing attenuation with decreasing temperature in the superconducting state as mentioned in feature (4).

It was possible to perform frequency-dependent measurements on the sample with $x=1$. The bell-shaped maximum moved to higher temperatures as the frequency was increased. This is indicative of a relaxation-type attenuation maximum. A model which attributes the attenuation to the relaxation of population changes in f-

electron energy levels induced by the propagation of sound in the sample, and which relates the attenuation to the Schottky specific heat will be reported elsewhere.[11] Here, let us concentrate on the attenuation variations in the superconducting state.

The attenuation in the superconducting state of samples $x=0.813$ and 0.6 increases when the temperature decreases from T_{c1} to T_m. An applied magnetic field will decrease the attenuation in this temperature range as long as the magnitude of the field is below H_{c2}. When superconductivity is quenched either by changing the temperature or by applying a constant magnetic field larger than H_{c2}, the enhancement of attenuation and the steplike change disappear, and the resultant temperature-dependent attenuation curves are, qualitatively, pretty much the same as those of the nonsuperconducting samples ($x>0.9$). Therefore, the rise in attenuation in the superconducting state is associated with the superconductivity of the sample. Figure 2 shows that the attenuation initially decreases at constant temperature when an external magnetic field is applied and the sample is in the superconducting state. A minimum is observed at H_{c2}. Again this behavior is different from what

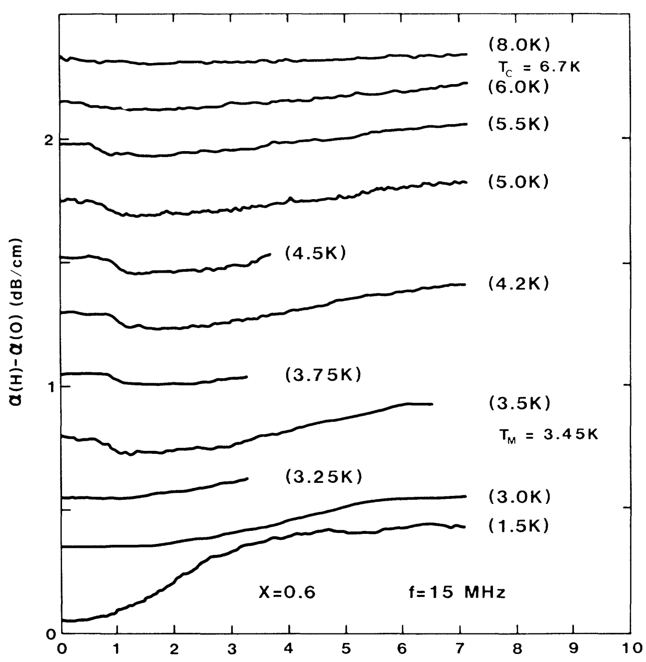

FIG. 2. $\alpha(H)$ for $Er_{0.4}Ho_{0.6}Rh_4B_4$ at constant temperatures. The curves have been shifted with respect to each other for clarity. The temperatures at which the curves were obtained are indicated on the right end of each curve. In zero field the sample is superconducting between 3.45 and 6.7 K, as displayed in the graph. For the curves obtained in this temperature range minima in attenuation occur when superconductivity is quenched at H_{c2}. All other curves display monotonic increases in attenuation as the magnetic field is increased.

is observed in either a type-I or -II superconductor, where the attenuation increases as a function of applied magnetic field.

$ErRh_4B_4$ is a well investigated reentrant superconductor. The ferromagnetic ordering of Er^{3+} ions occurring in the superconducting state eventually destroys superconductivity and returns the metal to the normal state at T_{c2}. Because large critical spin fluctuations appear at temperatures close to T_{c2} and T_m ($T_m > T_{c2}$), the attenuation increases near T_{c2} through spin-phonon coupling.

While it may be possible that the increase in attenuation in the Ho-rich superconducting samples is due to spin-phonon interaction with critical spin fluctuations,[12-14] we should mention the possibility that it is the increase of the Er^{3+}-ion concentration which produces these critical spin fluctuations in the superconducting state. According to the phase diagram for T_{c1} and T_m vs x of this system,[4] the ferromagnetic phase transition temperature T_m of the Er^{3+} ions in all the $Er_{1-x}Ho_xRh_4B_4$ samples is below 0.96 K (T_m of polycrystalline $ErRh_4B_4$) and depends on x. As is shown by the attenuation of $ErRh_4B_4$, the temperature range within which the spins of the Er^{3+} ions begin to fluctuate is quite narrow and fairly near the T_m of $ErRh_4B_4$.[15] Thus the increase in attenuation may not be due to fluctuations associated with the Er^{3+} ions. If the sharp change of attenuation at 3.45 and 4.95 K for the samples with $x=0.6$ and 0.813, respectively, are truly caused by critical spin fluctuations, it is more reasonable to assume that they are the spin fluctuations of the Ho^{3+} ions before they are ordered. The existence of a superconducting state in the $ErRh_4B_4$ sample is attributed to the weak exchange interaction between conduction electrons and the well-localized f electrons of the Er^{3+} ions. Therefore, the addition of Er^{3+} ions should weaken the indirect exchange interaction of the Ho^{3+} ions, and may indirectly result in the appearance of spin fluctuations of the Ho^{3+} ions.

To qualitatively explain the observed results in the superconducting state, we suggest the following two models. One model proposes that crystalline electric fields (CEF) in the samples of $Er_{1-x}Ho_xRh_4B_4$ align the magnetic moments of Ho^{3+} ions along the tetragonal c axis,[8] and suppress completely their spin fluctuations at temperatures close to the T_m of the samples with $x>0.9$. As the concentration of Er^{3+} ions becomes large enough to allow superconductivity to exist, the supercurrents will induce spin fluctuations.[16] This allows the suppressed spin fluctuations to be activated at temperatures close to the magnetic transition temperature T_m of the Ho^{3+} ions. However, these critical spin fluctuations do not show their full strength because they are also screened to some extent.[14] When an external magnetic field is applied, it depresses superconductivity and consequently spin fluctuations. As its magnitude reaches H_{c2}, the magnetic field destroys superconductivity, magnetizes the sample, and quenches spin fluctuations. In fact, field-dependent attenuation curves of samples with $x=0.6$ (Fig. 2) and $x=0.813$ show a minimum or very close to a minimum value at H_{c2}.

Another model which could account for the increase in attenuation in the superconducting state could be that the BCS coherence factor, which cancels the singularity in the density of states at the gap edge for electron-phonon interaction, does not do so in a magnetically reentrant superconductor because the electron spins are flipped for a magnetically mediated electron-phonon interaction and therefore the coherence factor has the opposite sign. The attenuation is proportional to the real part of the conductivity in the superconducting state σ_I, which for the latter case and a BCS value for the energy gap exhibits a maximum immediately below T_c and an exponential decay at lower temperatures.[17] However, recent calculations have shown that for energy gaps that are smaller than the BCS value of $2\Delta=3.52kT_c$ it is possible to obtain a broad maximum in σ_I which extends below $T_c/2$.[18] Since T_m is above $T_c/2$ in the samples shown in Fig. 1, the interaction is quenched before the attenuation starts to decrease in the superconducting state.

In summary, we have shown that the attenuation increase in samples with $x=0.6$ and 0.813 is associated with the presence of the superconducting state and may be caused by phonon interaction with spin fluctuations or by the BCS coherence factor associated with spin-mediated electron-phonon interaction in the superconducting state. We have also observed a broad attenuation maximum whose position moves to lower temperature as the Ho concentration is decreased.

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[1]M. B. Maple, in *Advances in Superconductivity,* edited by B. Deaver and J. Ruvalds (Plenum, New York, 1983), p. 279.

[2]L. D. Woolf, D. C. Johnston, H. B. Mackay, R. W. McCallum, and M. B. Maple, J. Low Temp. Phys. **35**, 651 (1979).

[3]H. R. Ott, L. D. Woolf, M. B. Maple, D. C. Johnston, and H. A. Mook, Phys. Rev. B **25**, 477 (1982).

[4]D. C. Johnston, W. A. Fertig, M. B. Maple, and B. T. Matthias, Solid State Commun. **26**, 141 (1978).

[5]The critical concentration of x was reported as 0.89 in Ref. 4, but in a recent paper [J. W. Lynn, A. Gotaas, R. N. Shelton, H. E. Horng, and C. J. Glinka, Phys. Rev. B **31**, 5756 (1985)] this critical concentration is 0.9.

[6]H. B. Mackay, L. D. Woolf, M. B. Maple, and D. C. Johnston, Phys. Rev. Lett. **42**, 918 (1979).

[7]H. A. Mook, W. C. Koehler, M. B. Maple, Z. Fisk, D. C. Johnston, and L. D. Woolf, Phys. Rev. B **25**, 372 (1982).

[8]B. D. Dunlap and D. Niarchos, Solid State Commun. **44**, 1577 (1982); H. B. Radousky, B. D. Dunlap, G. S. Knapp, and D. G. Niarchos, Phys. Rev. B **27**, 5526 (1983).

[9]D. E. Moncton, D. B. Mowhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. **39**, 1164 (1977).

[10]G. H. Lander, S. K. Sinha, and F. Y. Fradin, J. Appl. Phys. **50**, 1990 (1979).

[11]K. J. Sun, R. S. Sorbello, and M. Levy, Phys. Rev. B (to be published).

[12]M. Tachiki, M. C. Lee, and M. Levy, Phys. Rev. Lett. **29**, 488 (1972); S. Maekawa, R. A. Treder, M. Tachiki, M. C. Lee, and M. Levy, Phys. Rev. B **13**, 1284 (1976).

[13]R. A. Treder, M. Tachiki, and M. Levy, J. Magn. Magn. Mater. **12**, 167 (1979); R. A. Treder and M. Levy, J. Magn. Magn. Mater. **5**, 9 (1977).

[14]K. J. Sun, M. Levy, M. B. Maple, and M. S. Torikachvilli, *Ultrasonics Symposium Proceedings, 1983,* edited by B. R. McAvoy (IEEE, New York, 1983), p. 1087.

[15]K. J. Sun, M. Levy, M. B. Maple, and M. S. Torikachvilli (to be published).

[16]This assumption has a serious flaw since it implies that supercurrents may shield the CEF. However, the CEF are very short ranged while supercurrent screening is usually only effective for long range. It may be possible that a self-consistent model which includes the effect of fluctuations on supercurrent screening has to be developed in order to properly assess the validity of the phenomenological model being discussed in this paragraph.

[17]M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), pp. 50–59.

[18]H. P. Baum, A. Schenstrom, Y. Zheng, B. K. Sarma, and M. Levy, IEEE Trans. Magn. (to be published).