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Elastic Properties of Superconducting Stannides: $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$

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We present an experimental investigation of the temperature and magnetic field dependence of the elastic constants in the two stannide compounds $Yb_3Rh_4Sn_{13}$ *and* $Ca_3Rh_4Sn_{13}$. *We find a small elastic softening of the* c_{44} *mode of ca. 2% in the normal state. The temperature dependence of the various elastic modes are quite anomalous in the superconducting state. A comparison of our results is given with corresponding results of* $CeRu_2$, *an amorphous superconductor and other amorphous materials.*

I. INTRODUCTION

We present elastic constant, magnetization and ultrasonic attenuation measurements of cubic ternary stannides $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$. This is part of a programme investigating the normal and superconducting state by ultrasonic methods. In the past we have dealt with heavy fermion superconductors,[1] Chevrel phase compounds,[2] $CeRu_2$,[3] HfV_2,[4] and $Ba_{1-x}K_xBiO_3$.[5] The prominent features for the latter class of superconductors were a strong softening with respect to temperature of some symmetry elastic constants (c_{44}, $c_{11}-c_{12}$) in the normal state ($PbMo_6S_8$, $Eu_{0.6}Sn_{0.4}Mo_6S_8Br_{0.1}$, $CeRu_2$, HfV_2) and a pronounced peak effect (as encountered in many type II superconductors and observed in magnetization and magnetostriction measurements for $B < B_{c2}$) also observed in acoustic measurements for $CeRu_2$ and $Ba_{1-x}K_xBiO_3$.

We will discuss similar features in the stannide compounds $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$. These systems with superconducting transition temperatures of 7–8 K were recently investigated using magnetization and transport measurements especially with respect to superconducting properties, mainly the peak effect.[6,7] These experimental results show striking similarities with analogous results in $CeRu_2$.[8] In the present investigation we will show that the acoustic properties differ considerably from the ones in $CeRu_2$ partly because the electron-phonon coupling is much stronger in the latter. Therefore we cannot perform the detailed experiments which were done in $CeRu_2$ (Refs. 3 and 9) elucidating the interaction of a structural and superconducting transition and the detailed analysis of the peak effect using ultrasonic techniques.

In the following chapters we present some experimental details, results on the normal state and the superconducting properties for the two stannide compounds.

II. EXPERIMENT

The compounds $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$ belong to the family of ternary stannides. They form a phase I (primitive cubic) with two inequivalent sites for the Sn atoms: $Sn(1)Yb_3Rh_4Sn(2)_{12}$ where $Sn(1)Yb_3$ forms a A-15 type sublattice. These compounds can have a slight modification due to a disorder of the Yb or Ca and Sn(1) sites.[10] In our acoustic measurements we do also observe an indication of such a disorder for both compounds by a comparison with amorphous superconductors and quasicrystals. The single crystals were grown by a Sn flux method.[11] Sound velocity and ultrasonic attenuation were measured using a phase sensitive detection scheme[1] employed for numerous experiments before. Quartz and $LiNbO_3$ transducers and piezoelectric foils in the frequency range 6–180 MHz were used. The resolution was $1:10^6$ for relative and 2% for absolute sound velocity measurements. Our experiments were performed in a ^{4}He-cryostat (1.5–300 K) and in a toploading dilution refrigerator (50 mK–1 K). The dc magnetization was determined using a vibrating coil magnetometer. The single crystals for the two compounds had typical dimensions $2 \times 2 \times 3$ mm^3.

Relevant physical parameters for the single crystals used in this work and deduced from our experiments are given in Table I.

III. NORMAL STATE PROPERTIES

In Fig. 1 we present the temperature dependence of the elastic constants $c_L = (c_{11} + c_{12} + 2c_{44})/2$, $(c_{11} - c_{12})/2$ and c_{44} for the two compounds. It is seen that c_{44} exhibits the most anomalous effect, a softening of about 2% for both substances from room temperature down to low temperatures. For $(c_{11} - c_{12})/2$ similar effects are barely noticeable for the Yb-compound and a softening of only 0.3% below 50 K for the Ca-compound. For the longitudinal mode c_L in [110] direction the softening can be explained by the

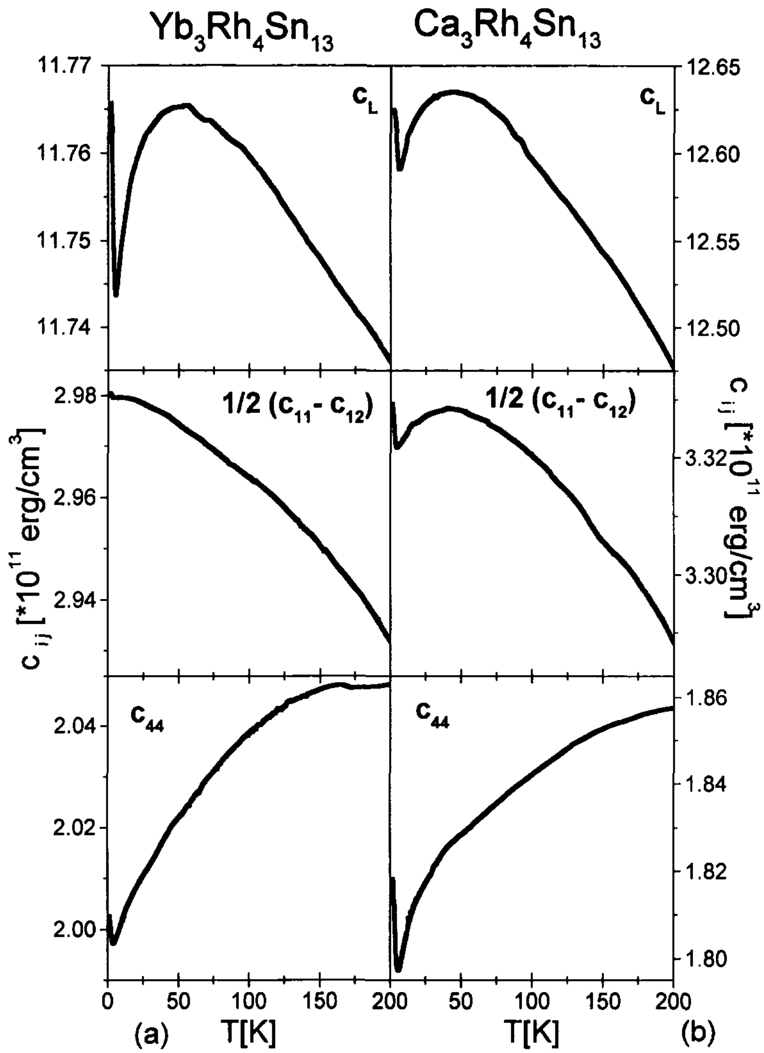

Fig. 1. (a) Temperature dependence of the elastic constants of $Yb_3Rh_4Sn_{13}$. (b) Temperature dependence of the elastic constants of $Ca_3Rh_4Sn_{13}$.

dominant c_{44} softening. The low temperature part of the elastic constants are shown later in greater detail in the section on superconductivity (Fig. 3).

These results have to be compared with analogous results for $CeRu_2$ where one finds, e.g., for $(c_{11} - c_{12})/2$ a total softening of 65% and a correspondingly smaller one for the other modes.[3, 9, 12] $CeRu_2$ is close to a cubic-tetragonal transition as discussed in ref. 3. Indeed under pressure one finds such a transition.[13] The corresponding results for our stannide crystals point to no structural effects. The deformation potential coupling constant for the c_{44} mode had to be at least $8\times$ larger to induce a cubic—trigonal transition. This estimate assumes the same density of states at the Fermi energy as for $CeRu_2$. Because of the nonavailability of band structure calculations we do not attempt a similar deformation potential fit to the

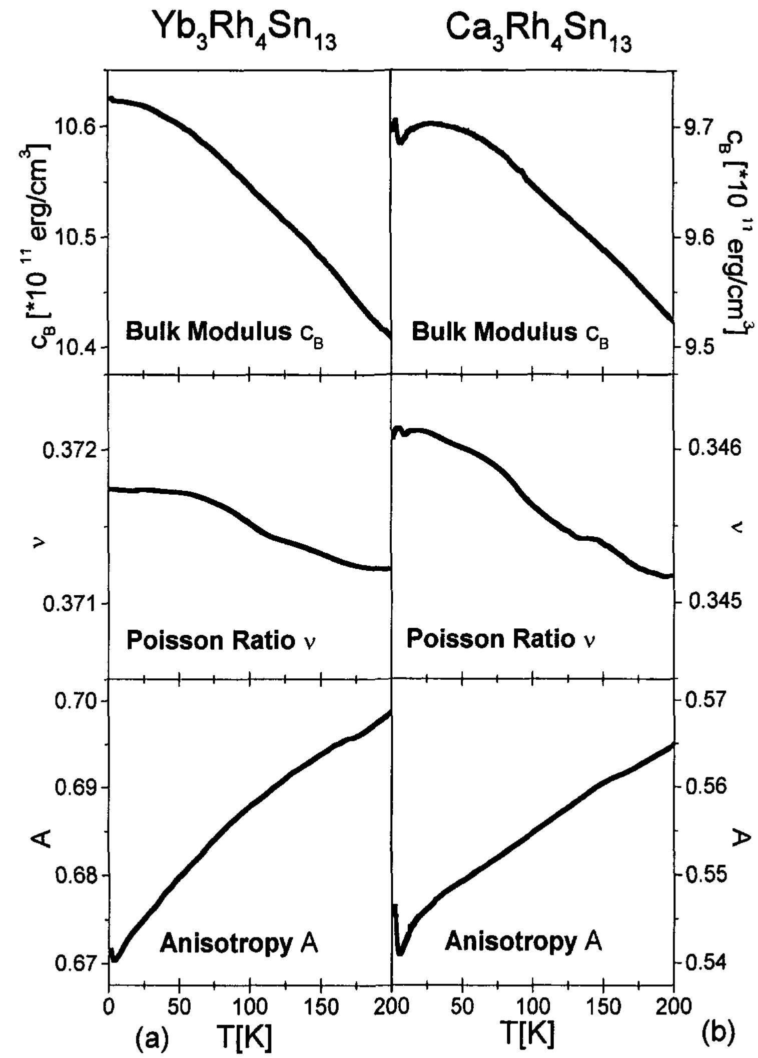

Fig. 2. Temperature dependence of the bulk modulus c_B, the Poisson ratio ν and the elastic anisotropy A. (a) $Yb_3Rh_4Sn_{13}$, (b) $Ca_3Rh_4Sn_{13}$.

Table I

Physical quantity	$Yb_3Rh_4Sn_{13}$	$Ca_3Rh_4Sn_{13}$
Density (g/cm^3)	8.9	8.3
c_{11} (10^{11} erg/cm^3) ($T = 200$ K)	12.62	13.91
c_{12} (10^{11} erg/cm^3) ($T = 200$ K)	6.77	7.33
c_{44} (10^{11} erg/cm^3) ($T = 200$ K)	2.05	1.86
Debye temp. Θ (from c_{ij})	195 K	218 K
T_c	6.5 K	7.1 K

experimental data as in $CeRu_2$. Note that the Sommerfeld coefficient γ is about the same for the compounds $CeRu_2$ and $Yb_3Rh_4Sn_{13}$ namely $\gamma \propto 28$ mJ/K^{2}mole.

In Fig. 2 we show the bulk modulus $c_B = (c_{11} + 2c_{12})/3$, the Poisson ratio $\nu = c_{12}/(c_{11} + c_{12})$ and the elastic anisotropy $A = 2c_{44}/(c_{11} - c_{12})$ for the Yb and Ca compounds. The first two quantities tell us something about the valence state of these compounds.[14] In valence fluctuating compounds ν should attain negative values and c_B should tend to zero at the valence transition. The fact that both c_B and ν have strongly positive values with $\nu > 0.3$ and a normal temperature dependence indicates that for both compounds the Yb-ion and the Ca-ion have a valency of 2+ and the Yb-ion is nonmagnetic (a full f shell). The same conclusion we reached before for $CeRu_2$,[3] namely that this compound is not a valence fluctuator but has a Ce^{4+}-ion with a full $4f$ shell, a fact which apparently is not generally known. Both stannide compounds are much more elastically isotropic than $CeRu_2$ as shown by the elastic anisotropy parameter A which is of order 0.6 in both compounds. The temperature dependence of A is rather small.

In Table I we gather all the constants deduced from our experiment. From the elastic constants we gain the Debye temperature Θ.[15] The values obtained can be compared with the ones deduced from specific heat experiments in $Yb_3Rh_4Sn_{13}$ (Ref. 16) $\Theta = 158$ K. Both determinations point to a Debye temperature comparable to the one for $CeRu_2$.

IV. SUPERCONDUCTING PROPERTIES

The temperature dependence of the sound velocities below 20 K covering also the $T < T_c$ region is given in Fig. 3. We measured down to 1.5 K with the exception of the longitudinal modes c_L and c_{11} where we present also data down to 50 mK taken in the dilution refrigerator. In the figure we present data for $B = 0$ T and $B > B_{c2}$. In the temperature region $T > 7$ K

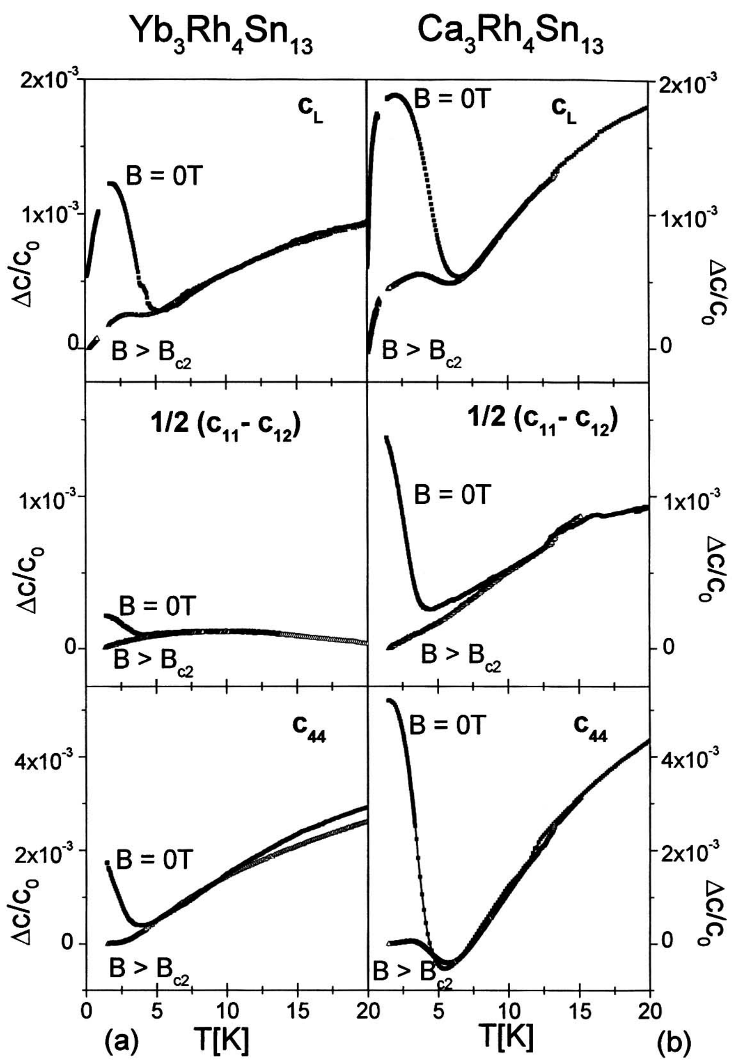

Fig. 3. Relative elastic constant changes for $Yb_3Rh_4Sn_{13}$ and $Ca_3Rh_4Sn_{13}$ in the low temperature region 50 mK $< T <$ 20 K for the different modes. The magnetic field direction gives // and ⊥ to the sound propagation the same result. Typical field values are $B \approx 3.5$–5 T.

the data correspond to the ones discussed in Sec. III. For $T < 5$ K we see an increase of the zero field sound velocity of relative magnitude of the order of 10^{-3}. These results have a peak around 1.5 K, which is clearly seen for the c_L mode. This maximum is almost completely suppressed with a magnetic field $B > B_{c2}$ as shown in the figures. The increase of the sound velocity in the superconducting regime is similar to the one occuring in the Chevrel compounds[2] except that a magnetic field has a much smaller effect for the latter because of the much larger B_{c2}. The size of the superconducting effects scale nicely with the corresponding ones in the normal state with the c_{44} modes exhibiting the largest effects. The results for $B > B_{c2}$ are the same for $B \parallel k$ and $B \perp k$, k being the acoustic wave vector.

We do not find a steplike decrease in the sound velocities as seen, e.g., in heavy fermion substances.[1,17] The reason is the same as for the related compounds $CeRu_2$ or Chevrel phases. It is the small strain-order parameter coupling constant which prevents the formation of a step like change in the elastic constant at T_c.

We do not have an explanation for the increase and the subsequent decrease of the sound velocity in the superconducting regime except to note that such effects have been observed before: In the sintered materials of the Chevrel phases[2] as noted above (see Fig. 4e) and more recently in the superconducting amorphous alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ (Ref. 18) where a two level model could describe these features. Similar effects have been found in vitreous silica, amorphous substances and even polycristalline materials[19] and in quasicrystals at low temperatures.[20] One might speculate about related physics in our case. If one plots the elastic constant changes logarithmically as a function of temperature (Fig. 4) for the Yb and Ca compounds one can see an approximate dependence proportional to $\ln T$ for all the different temperature intervals ($B = 0$ T increasing and decreasing branch, $B > B_{c2}$ increasing branch). Such kind of behaviour seems to indicate the existence of two level systems[18,21] but see the introductory remarks in ref. 19. From Fig. 4 it is seen that the sections with the linear $\ln T$ dependence increase with reduced power levels of the acoustic intensity at the lowest temperatures $T < 0.2$ K, which indicates probably self heating effects as noted before.[18] The normal state curve ($B > B_{c2}$) does respectively does not intersect with the superconducting curve for c_{11} and for c_L similar to the amorphous superconductor mentioned above.[18] The existence of the two level systems in these compounds might be due to a disorder of Sn(1) and Yb or Ca sites[10] as mentioned in Sec. II. Our low temperature results give however strong indications that such disorder is existent.

In Fig. 4d we show also an attenuation result for the Ca-compound. It is seen that $\alpha_s - \alpha_n$ increases just below T_c and has a steep fall before increasing again at low temperatures. The maximum attenuation just below T_c could be due to a coherence effect. In any case also the attenuation results show anomalous features in the superconducting region.

In Fig. 5 we present the magnetic field dependence of the relative elastic constant changes for the various modes in the superconducting

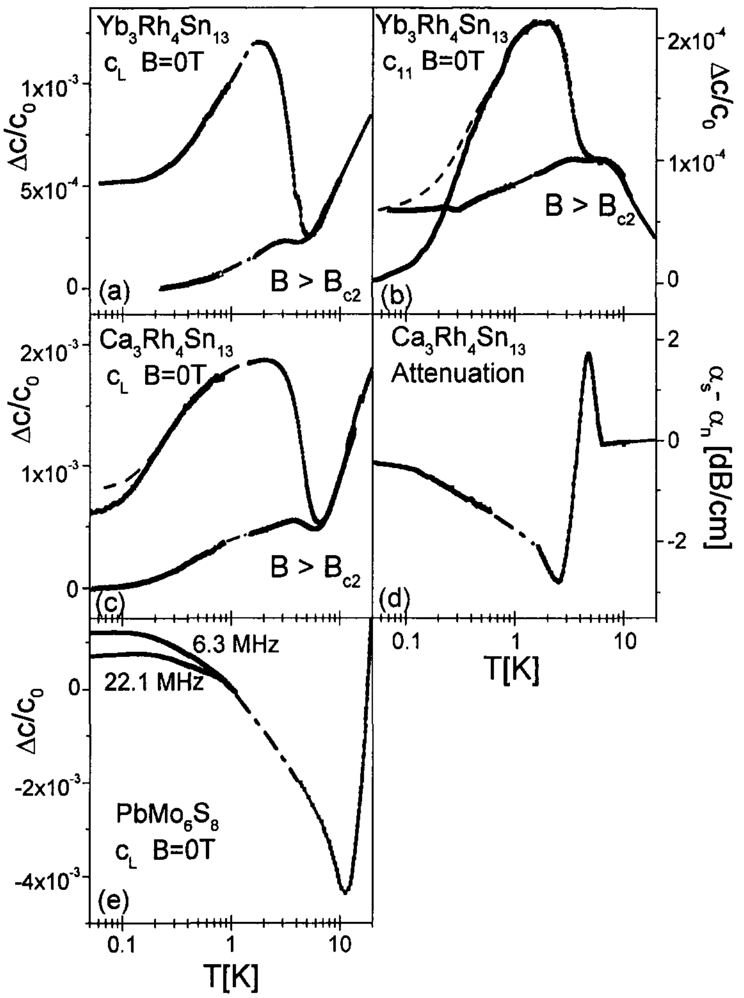

Fig. 4. Relative longitudinal elastic constant changes and attenuation plotted versus the logarithm of T for $B=0$ and $B>B_{c2}$. (a) c_L for $Yb_3Rh_4Sn_{13}$, (b) c_{11} for $Yb_3Rh_4Sn_{13}$, (c) c_L for $Ca_3Rh_4Sn_{13}$, (d) attenuation $\alpha_s-\alpha_n$ for $Ca_3Rh_4Sn_{13}$ for c_L mode from Fig. 4c (64 MHz), (e) Chevrel phase compound $PbMo_6S_8$, c_L from Ref. 2. The dashed lines in Fig.4 (b, c) indicate measurements at higher acoustic power, the dashed-dotted lines are a guide to the eye.

phase. Clearly the sound velocity change is negative as deduced from Fig. 3. The changes are stronger for the Ca-compound. The biggest change we have again for the c_{44} mode as in the normal state. In Fig. 5 we notice a small anomaly for the different isotherms right at the point beyond which the sound velocity is practically field independent. These points we identify

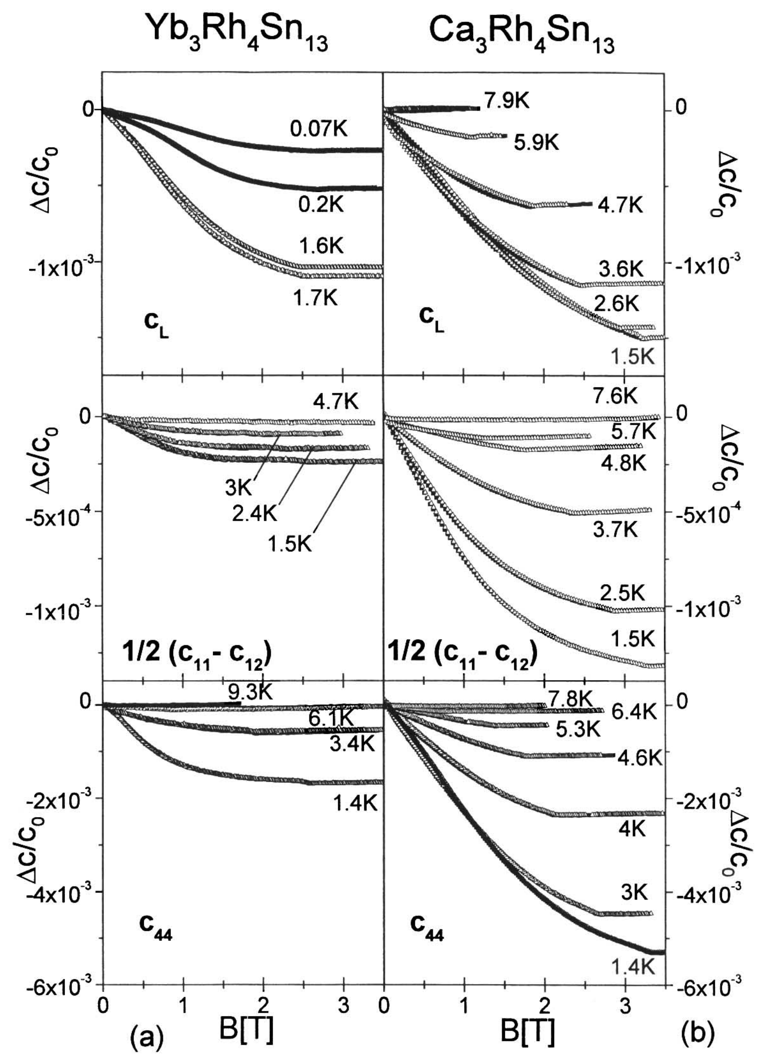

Fig. 5. Elastic constant isotherms as a function of magnetic field in the low temperature region 65 mK $< T <$ 10 K for c_L, $(c_{11}-c_{12})/2$ and c_{44}. All data are for $B // k$.

with the critical field B_{c2}. This empirical determination agrees very nicely with the result of magnetic measurements as shown in Fig. 7 and previous magnetic measurements.[6, 7] The temperature and field dependence of the sound velocity in the superconducting state is completely different from the case of $CeRu_2$ and not understood at all. We conjecture by analogy to similar effects observed in amorphous and polycristalline materials[19] that possible disorder effects are important in our case too.

As to the peak effect observed in magnetic measurements for these compounds, we can hardly see an analogous effect in elastic measurements. With the c_{44} mode one observes a slight indication in the field region where it is observed in the magnetic measurements. The effect is however rather small slightly above the limit of resolution. In Fig. 6 we show the peak effect deduced from magnetic measurements and acoustically for the c_{44} mode in $Yb_3Rh_4Sn_{13}$. While the magnetic effect is rather pronounced and similar to previous measurements[6, 16] the acoustic effect is rather small, of the order of 10^{-5}. We can estimate the size of the effect by comparison to $CeRu_2$. In this latter compound we have an overall peak effect for the c_{44} mode of 3×10^{-4} for the relative sound velocity. In $Yb_3Rh_4Sn_{13}$ we get for the same quantity an upper limit of 2×10^{-5}. Note that for $CeRu_2$ the c_{44}

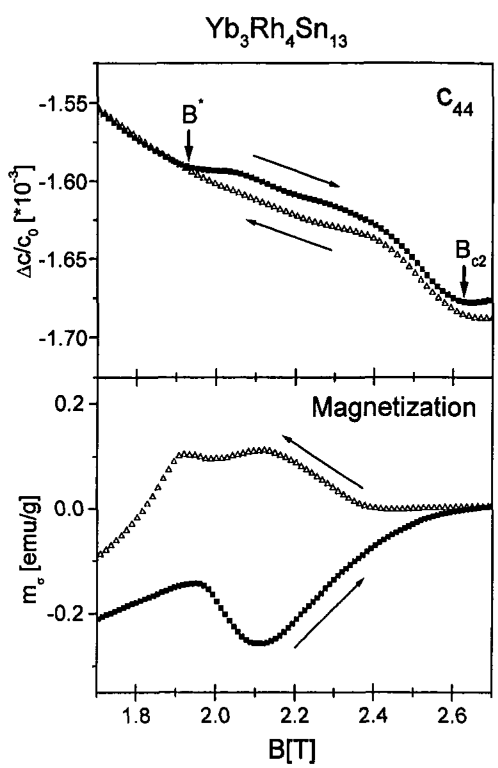

Fig. 6. Magnetic and acoustic peak effect in $Yb_3Rh_4Sn_{13}$. The determination of B_{c2} and B^* is indicated in the figure. The temperature is $T = 1.5$ K.

mode is not the mode with the strongest electron-phonon coupling (it is $c_{11} - c_{12}$), but for the Yb compound it is the mode with the strongest coupling. Therefore we get again a deformation potential coupling ratio between the corresponding modes c_{44} of the two substances of ca. 10 as we deduced from the normal state properties. So it is difficult to investigate peak effects in these stannide compounds with acoustic waves in detail.

In Fig. 7 we show the *B*–*T* phase diagramm as determined from our ultrasonic and magnetic measurements from Fig. 5 as discussed above. Previous results[6,7] agree nicely with our measurements. It is seen that the B_{c2} curve determined from ultrasonics is in good agreement with the magnetization results and previous magnetic measurements.[6,16] The superconducting parameters (coherence length, Ginzburg–Landau parameter etc.) are therefore the same and have been discussed already before.[16]

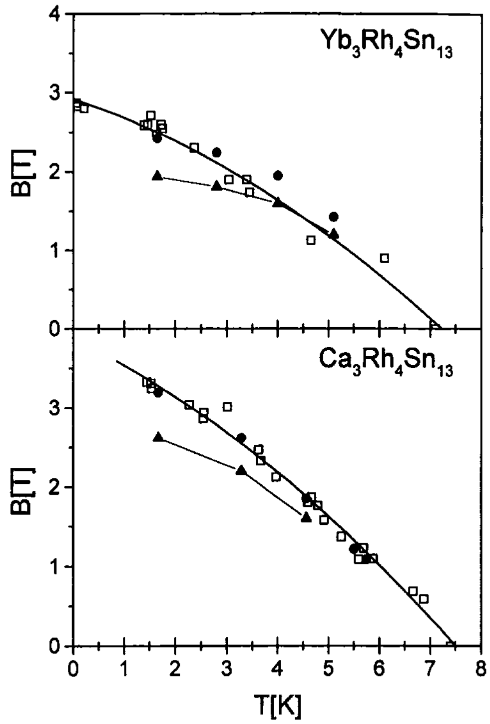

Fig. 7. *B*–*T* phase diagram deduced from elastic constant and magnetization measurements for the Yb and Ca compounds. Open squares: B_{c2} from kink in ultrasound, full circles: B_{c2} from magnetization, triangles: B^* from magnetization as defined in Fig. 6. The lines are guides to the eye.

V. CONCLUSIONS

We gave experimental evidence for a slight temperature softening of the c_{44} mode in the stannide compounds. This softening is an order of magnitude smaller than in $CeRu_2$. We argue that the deformation potential coupling is rather small in these Yb- and Ca-compounds. The acoustically determined peak effect for $B < B_{c2}$ is also an order of magnitude smaller than in the case of $CeRu_2$. The superconducting properties presented in this paper are very unusual. They exhibit features rather uncommon for single crystals but rather found in amorphous and other disordered materials.

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