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### Title

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### Permalink

<https://escholarship.org/uc/item/86d8q1dp>

### Journal

Journal of Magnetism and Magnetic Materials, 47(FEB)

### ISSN

0304-8853

### Authors

Mock, R  
Hillebrands, B  
Schmidt, H  
[et al.](#)

### Publication Date

1985-02-01

### DOI

10.1016/0304-8853(85)90426-3

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Peer reviewed

## ELASTIC ANOMALIES IN INTERMEDIATE VALENCE RARE-EARTH INTERMETALLICS

R. MOCK, B. HILLEBRANDS, H. SCHMIDT, G. GÜNTHERODT

*II. Phys. Inst. <sup>+</sup>, Universität Köln, 5000 Cologne 41, Fed. Rep. Germany*

Z. FISK

*Los Alamos National Laboratory, Los Alamos, NM 87545, USA*

and A. MEYER

*L.M.S.E.S., Institut de Physique, Université Louis Pasteur, 67084 Strasbourg, France*

The bulk moduli  $c_B$  of Rare earth (R) and Actinide (A) intermetallics ( $R-Cu_2Si_2$ ,  $R-Rh_2$ ,  $R-Ru_2$ ,  $R-Be_{13}$ ,  $A-Be_{13}$ ) have been determined by means of Brillouin scattering. A softening of  $c_B$  is found in  $EuCu_2Si_2$ ,  $YbCu_2Si_2$ ,  $CeCu_2Si_2$  and  $CeRh_2$ , but not in  $UBe_{13}$ .  $CeRu_2$  shows a  $c_B$  twice as large as that of  $LaRu_2$ .

By means of an improved technique for Brillouin scattering, using a 3 + 3 pass tandem Fabry–Perot interferometer according to Sandercock [1], it has now become feasible to reliably measure bulk transverse and longitudinal acoustic sound velocities of metals. Thus we are able to determine the bulk modulus of both single crystals and polycrystals [2].

With the help of this method we have determined the bulk moduli  $c_B$  of various polycrystalline Rare earth (R) and Actinide (A) intermetallics ( $R-Cu_2Si_2$ ,  $R-Ru_2$ ,  $R-Rh_2$ , R- and  $A-Be_{13}$ ) with particular emphasis on intermediate valence effects. These should show up most pronounced in the bulk modulus because of the volume changes associated with  $4f^n \leftrightarrow 4f^{n-1} + e^-$  valence fluctuations. All measurements were carried out at room temperature. The  $c_B$  values of each series of compounds (except  $R-Ru_2$ ) have been plotted as functions of  $Q/V$ , where  $Q$  is the valence of the R or A ion and  $V$  is the unit cell volume. For stable valent compounds this should yield a linear dependence of  $c_B$  on  $Q/V$ , whereas the intermediate valence effects are indicated by deviations from this behavior.

Fig. 1 shows the results for  $R-Cu_2Si_2$ . Contrary to the stable valent  $R-Cu_2Si_2$  the compounds  $EuCu_2Si_2$  and  $YbCu_2Si_2$  exhibit a softening of the bulk modulus of 32 and 43%, respectively, with respect to the reference line. This softening is attributed to the  $4f^n \leftrightarrow$

$4f^{n-1} + e^-$  configurational mixing near the Fermi level [3–5] which causes the R ions, and thus in turn the lattice, to become more compressible. A comparison of our  $c_B$  values with those determined by X-ray diffraction under hydrostatic pressure [6–8] as given elsewhere [2] shows good agreement within the error bars.

The 14% softening of  $c_B$  of  $CeCu_2Si_2$  may also be associated with a valence instability effect, but even more so it may be indicative of the electron–phonon

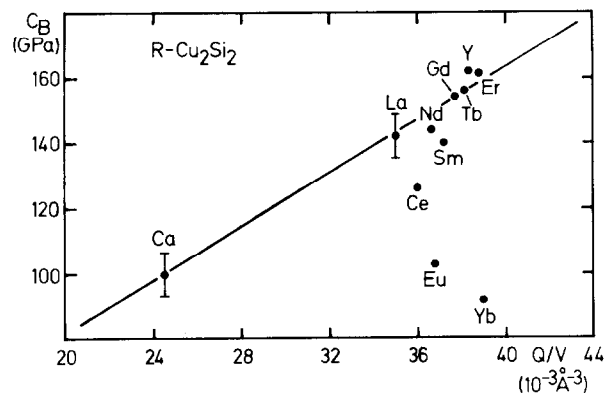


Fig. 1. Bulk modulus  $c_B$  of  $R-Cu_2Si_2$  vs. the ratio  $Q/V$  of the valence  $Q$  of the Rare earth (R) ion and the unit cell volume  $V$  of the lattice. The stable-valent  $R-Cu_2Si_2$  follow a linear  $c_B$  vs.  $Q/V$  relation.

<sup>+</sup> Work supported by DFG, SFB 125.

coupling in this “heavy-fermion” superconductor ( $T_c = 0.5$  K [9]). The large volume dependence of the spin-fluctuation or Kondo temperature ( $T^* = 10$  K [9]) has recently been considered as the dominant electron-phonon coupling mechanism in  $\text{CeCu}_2\text{Si}_2$  [10]. The softening of  $c_B$  is consistent with such a Kondo volume collapse-type of electron-phonon interaction.

An extraordinary situation is found in the case of the superconductor  $\text{CeRu}_2$  ( $T_c = 6.2$  K [11]). It turns out that  $c_B$  of  $\text{CeRu}_2$  is twice as large as that of the reference compound  $\text{LaRu}_2$  ( $\text{CeRu}_2$ :  $c_B = 134$  GPa,  $\text{LaRu}_2$ :  $c_B = 63$  GPa). An explanation for this behavior can be found in the valence of  $\text{CeRu}_2$ , which was determined by  $L_{III}$  X-ray absorption as  $\nu = 3 + \nu = 3.3$  [12]. On the basis of this valence and the superconducting properties of  $\text{CeRu}_2$  the Ce ion may be considered as in the  $\alpha'$ -Ce type phase [13], where the valence is not pressure-dependent ( $d\nu/dp = 0$ ). Thus in eq. 1

$$\frac{1}{c_B} = - \frac{1}{V} \frac{\partial V}{\partial p} \Big|_{\nu} - \frac{1}{V} \frac{\partial V}{\partial \nu} \Big|_p \frac{d\nu}{dp}, \quad (1)$$

the second term vanishes and therefore  $\text{CeRu}_2$  should show at least no softening in  $c_B$ , because the first term represents the “isovalent” contribution to the compressibility. Moreover, in the  $\alpha'$ -phase of Ce the valence becomes reduced as compared to the  $\alpha$ -phase of Ce [13], implying an increased volume of the Ce atom. Consequently, the  $\alpha'$ -Ce type ion in  $\text{CeRu}_2$  acquires a larger volume as compared to an  $\alpha$ -Ce type ion. On the other hand, the unit cell volume of  $\text{CeRu}_2$  is 6% smaller with respect to  $\text{LaRu}_2$  ( $\text{LaRu}_2$ :  $V = 457 \text{ \AA}^3$ ,  $\text{CeRu}_2$ :  $V = 428 \text{ \AA}^3$  [14]). As a consequence of the “external” and the very large “internal” pressure the bulk modulus of  $\text{CeRu}_2$  exceeds that of  $\text{LaRu}_2$  by a factor of two.

$\text{CeRh}_2$  has a valence of 3.24 [12], which raises the

question whether it is  $\alpha$ -Ce or  $\alpha'$ -Ce like [13] and might exhibit a similar behavior as  $\text{CeRu}_2$ . The bulk modulus of  $\text{CeRh}_2$  has been determined together with that of La-, Y- and  $\text{LuRh}_2$ . The  $c_B$  vs.  $Q/V$  plot in fig. 2 shows a 20% softening of  $c_B$  of  $\text{CeRh}_2$  with respect to the reference line of the stable valent R-Rh<sub>2</sub>. Hence we conclude that the behavior of  $\text{CeRh}_2$  resembles that of the  $\alpha$ -Ce phase where the valence increases with increasing external pressure [13], so that the softening of  $c_B$  is caused by the second term in eq. 1.

The series of R- and A-Be<sub>13</sub> intermetallics has been investigated in order to clarify whether  $c_B$  of intermediate valent  $\text{CeBe}_{13}$  is indeed larger than that of  $\text{LuBe}_{13}$  [15] and to determine  $c_B$  of the supposed p-wave superconductor  $\text{UBe}_{13}$  [16] ( $T_c = 0.85$  K [17]). The results of  $c_B$  vs.  $Q/V$  are shown in fig. 3. The overall magnitude of the  $c_B$  values in fig. 3 is of the order of  $c_B = 100$  GPa of Be. This is due to the fact that the Be atoms form cages around the R or A ions and in first order dominate the elastic behavior. For the presently available data a tentative reference line has been indicated in fig. 3 by the dashed line. The scaling between R- and A-Be<sub>13</sub> compounds has to be taken with some caution as seen by the behavior of their ( $q \approx 0$ ) optical phonon frequencies  $\hbar\omega_{\text{opt}}$  vs.  $Q/V$  [18]. (While the stable valent R-Be<sub>13</sub> show a linear variation of all  $\hbar\omega_{\text{opt}}$  vs.  $Q/V$ , particularly  $\text{ThBe}_{13}$  shows non-systematic deviations from this behavior.) The non-softening of  $c_B$  of intermediate valent  $\text{CeBe}_{13}$  at 300 K is somewhat puzzling, especially in view of its anomalous temperature dependence upon cooling below 300 K [15]. While the overall softening of  $c_B$  of  $\text{CeBe}_{13}$  between 300 and 0.5 K has been attributed to the effect of approaching a second-order  $\gamma$ - $\alpha$  Ce type phase transition because of

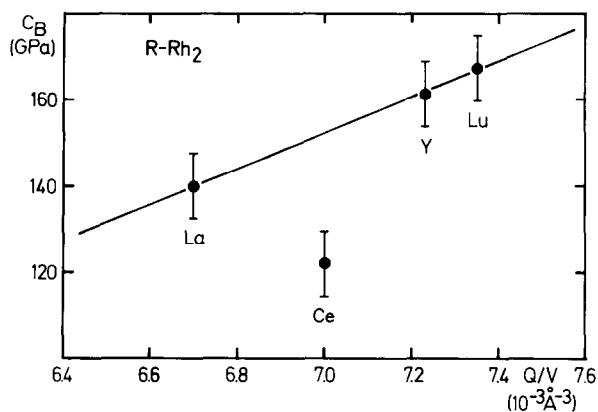


Fig. 2.  $c_B$  vs.  $Q/V$  of R-Rh<sub>2</sub> (R = rare earth).

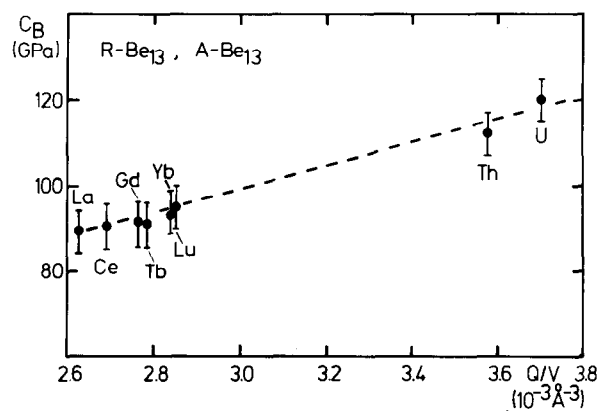


Fig. 3.  $c_B$  vs.  $Q/V$  of R- and A-Be<sub>13</sub> (R = rare earth, A = actinide).

the Ce dilution in the Be matrix [15,19], a magnetoelastic coupling of the volume strain to two distinct electronic states (possibly reminiscent of  $\Gamma_7$ - $\Gamma_8$  crystalline electric field excitations) has been used to explain the minimum in the temperature dependence of  $c_B$  near 135 K [20].

The “heavy-fermion” superconductor  $UBe_{13}$  shows no anomaly in  $c_B$ , even when assuming a horizontal reference line for the  $A$ - $Be_{13}$ . This result is in contrast to the behavior of  $CeCu_2Si_2$  and may be indicative of an electronic superconducting transition of  $UBe_{13}$  due to an interaction different from the usual electron-phonon interaction [16].

#### Acknowledgements

We would like to thank D. Wohlleben and J. Röhler for many stimulating and helpful discussions.

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