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**OPTICAL PHONON ANOMALY IN CeBe<sub>13</sub> AND Ce<sub>1-x</sub>La<sub>x</sub>Be<sub>13</sub>**

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The two ( $q \approx 0$ ) breathing ( $\Gamma_1^+$ ) modes of CeBe<sub>13</sub> show a softening with respect to the stable valence compounds. This softening increases upon Ce dilution in Ce<sub>1-x</sub>La<sub>x</sub>Be<sub>13</sub>. The latter shows for  $0 < x < 1.0$  a softening in all other symmetry modes which parallels the variation of the Debye temperature.

Intermediate Valence (IV) compounds are expected to exhibit phonon anomalies when the charge fluctuation rate  $h/\tau_c = \Gamma_c$  is of the order of particular phonon frequencies. The phonon modes involved should have preferentially local ( $\Gamma_1^+$ ) breathing symmetry. In the IV compounds CeSn<sub>3</sub> and CePd<sub>3</sub> with valences of  $v = 3.02$  and  $v = 3.23$  from L<sub>III</sub> spectroscopy [1], respectively, no significant phonon anomalies have been observed [2,3]. The reason may be that the calculated monopolar charge relaxation rate  $\Gamma_c$  of Ce [4], which increases strongly with decreasing valence towards Ce<sup>3+</sup>, is much higher than the highest optical phonon frequencies. On the other hand, the optical phonon modes of the light Be atoms in CeBe<sub>13</sub>, which has a valence of 3.04 at 300 K [1], should be at much higher frequencies and possibly comparable with  $\Gamma_c$ . At the same time an investigation of the electron-phonon coupling in the conjectured IV compound YbBe<sub>13</sub> [5] is of particular interest.

Here we report the first observation of the Raman-active phonon modes in the intermetallics RBe<sub>13</sub> (R = La, Ce, Gd, Tb, Yb, Lu) and Ce<sub>1-x</sub>La<sub>x</sub>Be<sub>13</sub> ( $x = 0.0, 0.1, 0.23, 0.55, 0.8, 1.0$ ). They crystallize in the cubic NaZn<sub>13</sub> structure (space group O<sub>h</sub><sup>6</sup>), exhibiting 10 ( $q \approx 0$ )

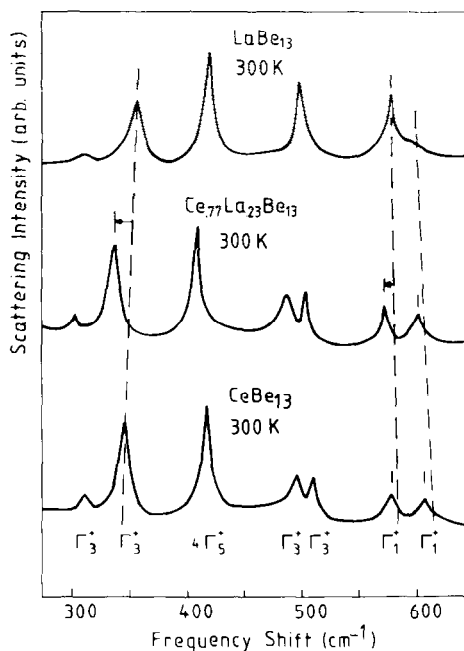


Fig. 1. Raman spectra of LaBe<sub>13</sub>, Ce<sub>0.77</sub>La<sub>0.23</sub>Be<sub>13</sub> at room temperature; the behavior of the stable valence reference compounds is indicated for three modes by the dashed lines.

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Raman-active modes:  $2\Gamma_1^+ + 4\Gamma_3^+ + 4\Gamma_5^+$ . In fig. 1 we show the Raman spectra of  $\text{LaBe}_{13}$ ,  $\text{CeBe}_{13}$  and  $\text{Ce}_{0.77}\text{La}_{0.23}\text{Be}_{13}$  at 300 K. We observe seven modes, except in  $\text{LaBe}_{13}$  where the two modes near  $500\text{ cm}^{-1}$  are degenerate. The spectra of the other samples, together with the polarization analysis for the mode symmetries will be given elsewhere [6]. The symmetry assignment of the seven modes is given at the bottom of fig. 1. The assignment of the two  $\Gamma_1^+$  breathing modes is corroborated by plotting the mode frequencies as a function of lattice parameter as shown in fig. 2 for the  $\text{RBe}_{13}$  series. The stable valent reference compounds  $\text{LaBe}_{13}$ ,  $\text{GdBe}_{13}$ ,  $\text{TbBe}_{13}$  and  $\text{LuBe}_{13}$  show a linear variation with lattice constant as indicated in fig. 2 by the solid lines. No anomaly is observed for  $\text{YbBe}_{13}$ . On the other hand, the two  $\Gamma_1^+$  modes of  $\text{CeBe}_{13}$  show a softening of about 2% with respect to the reference line. All other symmetry modes of  $\text{CeBe}_{13}$  do not show any anomaly. An even stronger softening of the two  $\Gamma_1^+$  modes is found upon Ce dilution in  $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$  as seen for  $x = 0.23$  in fig. 1 and for all measured compositions  $0.1 \leq x \leq 0.8$  in fig. 2. However, contrary to  $\text{CeBe}_{13}$ , this mode softening in  $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$  for  $0.1 \leq x \leq 0.8$  is also observed for all other symmetry modes with respect to the average behavior of the reference materi-

als. This is indicated for, e.g., the  $\Gamma_3^+$  mode of  $\text{Ce}_{0.77}\text{La}_{0.23}\text{Be}_{13}$  near  $340\text{ cm}^{-1}$  in fig. 1 with respect to the dashed reference line. The phonon softening in  $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$  for  $0.1 \leq x \leq 0.8$ , independent of the mode symmetry is also reflected by the behavior of the Debye temperature  $\theta_D$  [7] which is displayed at the bottom of fig. 2. No temperature dependent phonon anomaly has been observed for the optical phonons of  $\text{CeBe}_{13}$ , contrary to the anomalous softening of the bulk modulus upon cooling down below 350 K [8].

The two  $\Gamma_1^+$  modes are attributed to the long-wavelength breathing modes of either the 12  $\text{Be}_{11}$ -atom icosahedra around central  $\text{Be}_1$  atoms or of the 24  $\text{Be}_{11}$ -atom polyhedra around central R atoms. Since both  $\Gamma_1^+$  modes of  $\text{CeBe}_{13}$  show a softening this implies that the  $\text{Be}_1$ - $\text{Be}_{11}$  breathing motion is also felt by the Ce ions. By calibrating the theoretical ratio [4] of charge to spin relaxation rates by the experimental spin relaxation rate  $\Gamma_s/2 = 20\text{ meV}$  of  $\text{CeBe}_{13}$  [9] the charge relaxation rate exceeds the highest phonon frequencies by about a factor of ten. This manifests itself in the small softening (2%) of the two  $\Gamma_1^+$  modes of  $\text{CeBe}_{13}$  (see fig. 2). The dilution of Ce in  $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$  leads to a reduction of all relaxation rates, indicated by the decreasing susceptibility maximum [7]. Similarly, a reduction of the

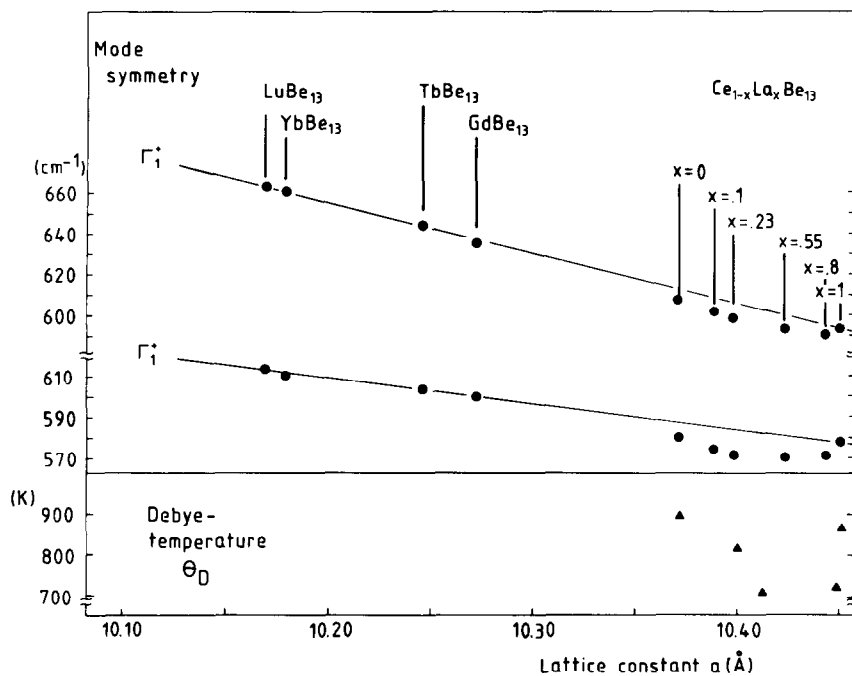


Fig. 2. Frequencies of the two  $\Gamma_1^+$  Raman-active modes and the Debye temperature  $\theta_D$  as a function of the lattice parameter for various  $\text{RBe}_{13}$  and  $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$  compounds.

fluctuation temperature  $T_f$  from  $\approx 150$  K ( $0.0 < x < 0.7$ ) to  $\approx 50$  K ( $x \geq 0.8$ ) has been deduced from thermal expansion measurements [10]. Consequently the charge relaxation rate will be lowered, coming closer to the optical phonon frequencies. This is reflected in the further softening of the  $\Gamma_1^+$  modes with increasing  $x$ . The concurrent softening of all other  $q \approx 0$  symmetry modes stems from their long-wavelength phase-coherent averaging over primarily local ( $\Gamma_1^+$ ) breathing-type charge fluctuations. This effect is obviously more pronounced for short-wavelength zone boundary phonons, which contribute most to  $\theta_D$  (see fig. 2) due to their high density of states.

In conclusion,  $CeBe_{13}$  shows a small softening of the two  $\Gamma_1^+$  ( $q \approx 0$ ) optical phonon breathing modes due to the considerably higher charge fluctuation rate. A lowering of this rate upon Ce dilution in  $Ce_{1-x}La_xBe_{13}$  results in a softening of all ( $q \approx 0$ ) optical phonon modes irrespective of their symmetries. A much larger softening is expected near the zone boundary and is reflected by that of  $\theta_D$  with increasing  $x$ . The absence of any optical phonon anomaly of  $YbBe_{13}$  is consistent with the previous conclusions about its stable  $3 +$  valence state [11].

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