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OPTICAL PHONON ANOMALY IN CeBe_{13} AND $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$

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The two ($q \approx 0$) breathing (Γ_1^+) modes of CeBe_{13} show a softening with respect to the stable valence compounds. This softening increases upon Ce dilution in $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$. 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 $\hbar/\tau_c = \Gamma_c$ is of the order of particular phonon frequencies. The phonon modes involved should have preferentially local (Γ_1^+) breathing symmetry. In the IV compounds CeSn_3 and CePd_3 with valences of $v = 3.02$ and $v = 3.23$ from L_{III} spectroscopy [1], respectively, no significant phonon anomalies have been observed [2,3]. The reason may be that the calculated monopolar charge relaxation rate Γ_c of Ce [4], which increases strongly with decreasing valence towards Ce^{3+} , is much higher than the highest optical phonon frequencies. On the other hand, the optical phonon modes of the light Be atoms in CeBe_{13} , which has a valence of 3.04 at 300 K [1], should be at much higher frequencies and possibly comparable with Γ_c . At the same time an investigation of the electron–phonon coupling in the conjectured IV compound YbBe_{13} [5] is of particular interest.

Here we report the first observation of the Raman-active phonon modes in the intermetallics RBe_{13} ($\text{R} = \text{La, Ce, Gd, Tb, Yb, Lu}$) and $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$ ($x = 0.0, 0.1, 0.23, 0.55, 0.8, 1.0$). They crystallize in the cubic NaZn_{13} structure (space group O_h^6), exhibiting 10 ($q \approx 0$)

Fig. 1. Raman spectra of LaBe_{13} , $\text{Ce}_{0.77}\text{La}_{0.23}\text{Be}_{13}$ 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 LaBe_{13} , CeBe_{13} and $\text{Ce}_{0.77}\text{La}_{0.23}\text{Be}_{13}$ at 300 K. We observe seven modes, except in LaBe_{13} where the two modes near 500 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 Γ_1^+ breathing modes is corroborated by plotting the mode frequencies as a function of lattice parameter as shown in fig. 2 for the RBe_{13} series. The stable valent reference compounds LaBe_{13} , GdBe_{13} , TbBe_{13} and LuBe_{13} show a linear variation with lattice constant as indicated in fig. 2 by the solid lines. No anomaly is observed for YbBe_{13} . On the other hand, the two Γ_1^+ modes of CeBe_{13} show a softening of about 2% with respect to the reference line. All other symmetry modes of CeBe_{13} do not show any anomaly. An even stronger softening of the two Γ_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 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 Γ_3^+ mode of $\text{Ce}_{0.77}\text{La}_{0.23}\text{Be}_{13}$ near 340 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 θ_D [7] which is displayed at the bottom of fig. 2. No temperature dependent phonon anomaly has been observed for the optical phonons of CeBe_{13} , contrary to the anomalous softening of the bulk modulus upon cooling down below 350 K [8].

The two Γ_1^+ modes are attributed to the long-wavelength breathing modes of either the 12 Be_{II} -atom icosahedra around central Be_I atoms or of the 24 Be_{II} -atom polyhedra around central R atoms. Since both Γ_1^+ modes of CeBe_{13} show a softening this implies that the Be_I - Be_{II} 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 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 Γ_1^+ modes of 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 Γ_1^+ Raman-active modes and the Debye temperature θ_D as a function of the lattice parameter for various RBe_{13} and $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$ compounds.

fluctuation temperature T_f from ≈ 150 K ($0.0 < x < 0.7$) to ≈ 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 Γ_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 (Γ_1^+) breathing-type charge fluctuations. This effect is obviously more pronounced for short-wavelength zone boundary phonons, which contribute most to θ_D (see fig. 2) due to their high density of states.

In conclusion, CeBe_{13} shows a small softening of the two Γ_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 $\text{Ce}_{1-x}\text{La}_x\text{Be}_{13}$ 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 θ_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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