Valence changes in dicarbide solid solutions induced by structural changes

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The rare-earth metal carbides (REC\(_2\)) EuC\(_2\) and YbC\(_2\) are isostructural to alkaline-earth metal carbides (AEC\(_2\)), both containing C\(_2\) dumbbells. Despite their similar crystal structures completely different physical properties are observed, i.e. metallic (REC\(_2\)) versus insulating (AEC\(_2\)) behaviour. In this context, semiconducting properties with divalent Eu(II) under ambient conditions are found for EuC\(_2\)[1], but under pressure metallic EuC\(_2\) with trivalent Eu(III) is observed.[2] However, for YbC\(_2\) an intermediate valence of approx. 2.8 was determined.[3] As confirmed by XRPD data at RT we were able to synthesize several solid solutions by reaction of the elements, e.g. Yb\(_x\)Sr\(_{1-x}\)C\(_2\)[4], Eu\(_x\)Ca\(_{1-x}\)C\(_2\), Eu\(_x\)Ba\(_{1-x}\)C\(_2\) and Yb\(_x\)Ca\(_{1-x}\)C\(_2\)[4] (0 < x < 1). As a result, all solid solutions crystallize in different modifications depending on x. In addition, solid solutions containing Eu show a clear tendency towards a perfect vegard behaviour as reported for Eu\(_x\)Sr\(_{1-x}\)C\(_2\)[5], whereas solutions containing Yb show unusual effects that point to a change of Yb valence stimulated by composition, temperature and different crystal structures.