Valence Instabilities, Phase Transitions, and Abrupt Lattice Expansion at 5 K in the YbGaGe System

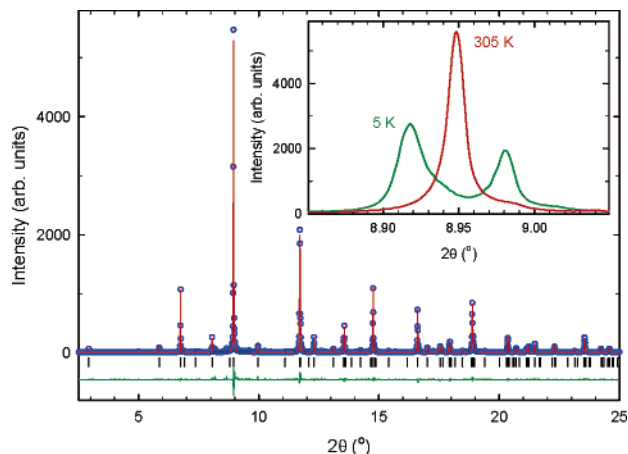Serena Margadonna,*,† Kosmas Prassides,*,‡ Andrew N. Fitch,§ James R. Salvador,‖ and Mercouri G. Kanatzidis*,‖

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Most materials exhibit positive thermal expansion coefficients, which lead to expanded lattices on heating. Negative thermal expansion (NTE), i.e., when the material contracts on heating, is relatively rare. It typically originates either from the presence of low-energy anharmonic lattice vibrations, which tend to contract the lattice on heating (e.g., in ZrW_2O_8),[1] or from the occurrence of continuous electronic valence transitions (e.g., in $Sm_{1-x}Gd_xS$[2] and $Sm_{2.75}C_{60}$).[3] Even rarer is the occurrence of zero thermal expansion (ZTE), whereupon the material neither expands nor contracts volumetrically over a broad temperature range. An example of a ZTE metallic conductor was recently provided by YbGaGe,[4] which shows negligible volume change between 100 and 400 K, as a result of a temperature-induced continuous valence transition from Yb^{2+} toward the smaller Yb^{3+} on heating. Deviations from the ideal stoichiometry are tolerated in the YbGaGe phase field, allowing the isolation of Ga- or Ge-rich compositions with stoichiometry $YbGa_{1+x}Ge_{1-x}$. Here we report that when we probed the structural properties of the Ga-rich composition, $YbGa_{1.05}Ge_{0.95}$, by high-resolution synchrotron X-ray diffraction, we found that contrary to the case of YbGaGe, it exhibits positive thermal expansion between 15 and 723 K. However, on further cooling to 5 K, an abrupt isosymmetric phase transition is encountered that is accompanied by a large volume increase on cooling (NTE) and is due to the sudden conversion of Yb^{3+} to the larger Yb^{2+}. After this volume expansion, the cell is larger than it was at room temperature. Complementary structural results on the isostructural YbGaSn analogue did not show such a transition.

Inspection of the synchrotron powder X-ray diffraction profiles of $YbGa_{1.05}Ge_{0.95}$[5] at various temperatures between 15 and 723 K readily reveals the hexagonal unit cell (space group $P6_3/mmc$) proposed before.[4] No reflections violating hexagonal extinction rules are evident, and the crystal structure is strictly hexagonal in this temperature range (Figure 1). However, a notable feature of the data is that both lattice constants, a and c, smoothly increase albeit at an anisotropic fashion on heating to 723 K, resulting in an overall volume expansion at a rate of $0.121(2)$ $Å^3$ K^{-1} (Figure 2a). This is in sharp contrast to the structural behavior of YbGaGe, in which the expansion on heating along the c axis was compensated by an associated contraction in the ab plane, thereby resulting in overall near-zero volumetric expansion.[4] Rietveld analysis of the diffraction profiles of YbGaSn between 4 and 473 K also proceeded smoothly with the same structural model, revealing again an anisotropic positive volume expansion at $0.129(2)$ $Å^3$ K^{-1} (at 300 K: $a = 4.44535(3)$ Å, $c = 17.3245(2)$ Å, Figures 1S and 2S).

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Figure 1. Final observed (○) and calculated (−) synchrotron X-ray diffraction profile for $YbGa_{1.05}Ge_{0.95}$ at 305 K ($a = 4.211170(8)$ Å, $c = 16.80480(7)$ Å, agreement factors of the Rietveld refinement: $R_{wp}= 7.09\%$, $R_{exp}= 1.21\%$, $R_{F2} = 5.63\%$). The lower solid line shows the difference profile, and the tick marks show the reflection positions. Inset: Selected region of the diffraction profile ($\lambda = 0.42970$ Å) of $YbGa_{1.05}Ge_{0.95}$ in the vicinity of (104) Bragg reflection at 5 and 305 K.

As the transition at 5 K sets in, *all* diffraction peaks in the diffraction profile of $YbGa_{1.05}Ge_{0.95}$ become accompanied by a partner at lower angle (Figure 1 inset), thereby providing the signature of a sudden (incomplete) transformation of the high-temperature structure to an isostructural one with significantly expanded lattice dimensions. Rietveld refinement of the diffraction data at 5 K was thus performed with a two-phase model to account for the coexisting phases. Both phases have the same hexagonal structure (space group $P6_3/mmc$) but with different lattice constants.[6] It is remarkable that the lattice expansion at 5 K is large enough to produce a cell volume comparable to that at $\sim$500 K. In contrast to $YbGa_{1.05}Ge_{0.95}$, no similar phase transformation was observed for YbGaSn down to 4 K (Figure 2S).[7]

Substantial changes to the diffraction profiles of $YbGa_{1.05}Ge_{0.95}$ are also observed on heating above 723 K. All hkl ($l \neq 0$) reflections gradually develop pronounced asymmetries on the high-angle side (Figure 4S) with peak shapes of the Warren functional type (sharp initial intensity increase followed by slow decay),[8] implying the development of marked disorder. The effect of temperature on the peak shape of the $hk0$ reflections is much less pronounced. The diffraction profiles remain extremely complex up to 1123 K, when both the peak asymmetries and the superlattice peaks disappear. All peaks then index to a simple hexagonal unit cell (space group $P6/mmm$) with lattice dimensions $a_0 \approx a$ and $c_0 \approx 1/4c$.[9] No comparable evolution of the structure of YbGaSn was observed on heating above 473 K, as this material begins to decompose.
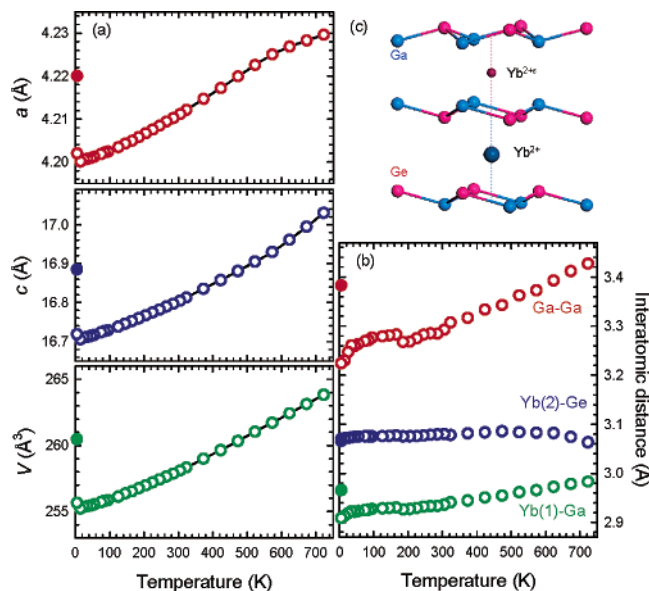
Figure 2. Temperature evolution of (a) the hexagonal lattice constants and the unit cell volume and (b) selected interatomic distances in YbGa$_{1.05}$-Ge$_{0.95}$. The abrupt lattice expansion at ~5 K is accompanied by equally abrupt increases in the Yb(1)−Ga and cross-layer Ga−Ga distances. (c) Building block of the layered YbGaGe structure.

The most prominent aspect arising from the results of the structural refinements is the remarkable lattice response of YbGa$_{1.05}$-Ge$_{0.95}$ at low temperatures. The negative thermal expansion and abrupt change in the unit cell metrics are not accompanied by a change in crystal symmetry, and the full space group is preserved. The origin of NTE behavior can be understood by referring to the details of the YbGa$_{1.05}$Ge$_{0.95}$ structure and the Yb valence. The crystal structure is characterized by the presence of puckered GaGe layers (Figure 2c) with alternating short and long interlayer spacings along the c axis of $d_1 = 3.899(3)$ Å and $d_2 = 4.454(3)$ Å, respectively (at 15 K). These sandwich two symmetry-inequivalent Yb ions. Yb(1) lies between the closely spaced layers bonding to six Ga atoms and was assigned an intermediate valence of $+(2 + \epsilon)$, while Yb(2) with a valence of $+2$ is between the more separated layers and bonds to six Ge atoms. If a valence transition of Yb(1) from $+(2 + \epsilon)$ toward $+2$, with a larger ionic size, occurs by depopulating the Ga $4p$ band as the sample is cooled to 5 K, the now larger Yb(1) will have a profound effect on the thickness of the GeGa−Yb(1)−GaGe slabs. This is indeed consistent with the observed equally abrupt and substantial expansion of the interlayer GaGe spacing d_1 from 3.899(3) to 4.051(8) Å within a few degrees of temperature and the concomitant volume increase of 2.03% (Figure 2a).

Another important point of the present work is that the thermal expansivity behavior of YbGa$_{1.05}$Ge$_{0.95}$ at higher temperatures contrasts sharply with that of YbGaGe,[4] implying that the elastic and electronic properties are highly sensitive to the exact stoichiometry. While YbGaGe shows a negligible volume change between 100 and 400 K, YbGa$_{1.05}$Ge$_{0.95}$ expands anisotropically but smoothly in the temperature range 15 to 723 K ($\delta V/V = 3.38\%$, $\alpha = 4.68(8) \times 10^{-5}$ K^{-1}). The thermal response of the lattice is comparable to that of YbGaSn, which also smoothly expands between 20 and 473 K by 2.01% ($\alpha = 4.37(6) \times 10^{-5}$ K^{-1}). Figure 2b shows the temperature dependence of selected interatomic distances for YbGa$_{1.05}$Ge$_{0.95}$. Besides the sharp discontinuities at 5 K for YbGa$_{1.05}$Ge$_{0.95}$, there is also a subtle decrease in the Ga−Ga and

Yb(1)−Ga distances on heating between 165 and 185 K that can be tentatively assigned to an additional slight increase in the Yb(1) valence state. The Yb(2)−Ge distance is constant from 5 to 180 K, consistent with our interpretation that the structural changes observed derive from electronic changes of Yb(1). However, increasing the temperature above ~400 K leads to a gradual shortening of the Yb(2)−Ge distance that may imply the occurrence of an additional electronic transition involving partial oxidation of Yb(2) from $+2$ toward $+(2 + \epsilon')$ with a smaller ionic size. On heating to 1123 K, the structure fully transforms to the AlB$_2$ structural type, comprising symmetry-equivalent isovalent Yb ions and flat disordered Ga/Ge layers with interlayer spacing of 4.343 Å. Work is in progress to understand the structural details between 723 and 1123 K, but it is logical to assume that the disorder signified by the complex peak shapes is associated with a gradually evolving distribution of short-range ordered domains with different c lattice constants.

In conclusion, the thermal expansion behavior of the YbGaGe system is very sensitive to slight deviations from stoichiometry. We have shown that YbGa$_{1.05}$Ge$_{0.95}$ displays a very complicated temperature-dependent structural and electronic phase diagram. NTE occurs but in an abrupt isosymmetric phase transition at 5 K to a significantly expanded lattice. The transition is unambiguously of electronic origin with strong coupling between the charge (valence) and lattice degrees of freedom. Additional subtle structural and electronic changes are apparent near 180 K and above 400 K until the material eventually collapses to a structure with equivalent Yb ions and flat Ga/Ge planes.

Supporting Information Available: Rietveld refinements of synchrotron X-ray diffraction profiles and refinement parameters. Temperature dependence of the lattice constants, unit cell volume, and selected interatomic parameters for YbGaSn (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References
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(5) YbGa$_{1.05}$Ge$_{0.95}$ and YbGaSn were prepared by solid-state reactions.[4] For the synchrotron X-ray diffraction measurements, the samples were sealed in thin-wall capillaries 0.5 mm in diameter. Diffraction data ($\lambda = 0.42970$ Å) were collected on heating at temperatures between 3 and 305 K (using a continuous-flow cryostat) and between 323 and 1123 K (using a furnace) in continuous scanning mode with the high-resolution multianalyzer powder diffractometer on beamline ID31 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The data were rebinned in the range 2.5−25° to a step of 0.001°. Data analysis was performed with the GSAS suite of Rietveld analysis programs. Some impurity peaks were excluded from the refinements.
(6) The refinement proceeded smoothly with the phase fraction of the expanded phase converging to 62.0(2)%. The results of the final refinement at 5 K are shown in Figure 3S ($R_{wp} = 9.67\%$, $R_{exp} = 1.76\%$, $R_{F2} = 7.85\%$, $a' = 4.22000(1)$ Å, $c' = 16.88466(9)$ Å, $a = 4.20169(1)$ Å, $c = 16.7175-(1)$ Å).
(7) A very small upturn in the unit cell size of YbGaSn between 20 and 4 K (~0.015%) may be the signature of a valence transition onset.
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(9) Stable Rietveld refinements were achieved with a structural model incorporating a single Yb ion and flat fully disordered Ga/Ge planes (AlB$_2$-type structure). The results of the final refinement at 1123 K are shown in Figure 5S ($R_{wp} = 8.35\%$, $R_{exp} = 3.28\%$, $R_{F2} = 5.55\%$, $a_0 = 4.231908-(3)$ Å, $c_0 = 4.342763(5)$ Å).

JA049728W