Zero thermal expansion in YbGaGe due to an electronic valence transition

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Most materials expand upon heating. Although rare, some materials expand on cooling, and are said to exhibit negative thermal expansion (NTE); but the property is exhibited in only one crystallographic direction. Such materials include silicon and germanium at very low temperature (<100 K) and, at room temperature, glasses in the titania–silica family, Kevlar, carbon fibres, anisotropic Invar Fe-Ni alloys, ZrW₂O₇ (ref. 4) and certain molecular networks. NTE materials can be combined with materials demonstrating a positive thermal expansion coefficient to fabricate composites exhibiting an overall zero thermal expansion (ZTE). ZTE materials are useful because they do not undergo thermal shock on rapid heating or cooling. The need for such composites could be avoided if ZTE materials were available in a pure form. Here we show that an electrically conductive intermetallic compound, YbGaGe, can exhibit nearly zero thermal expansion—that is, negligible volume change between 100 and 400 K. We suggest that this response is due to a temperature-induced valence transition in the Yb atoms. ZTE materials are desirable to prevent or reduce resulting strain or internal stresses in systems subject to large temperature fluctuations, such as in space applications and thermomechanical actuators.

YbGaGe and YbGaSn crystallize in the hexagonal P6₃/mmc space group (MoC₂ according to Pearson’s structure type)⁵ (see ref. 7 and references therein). The structure is a derivative of the MgB₂ structure type and is characterized by puckered boron nitride-like GaGe and GaSn layers (for example, A, B, C and D in Fig. 1a). In YbGaGe, the Ga and Ge positions could not be distinguished from the X-ray data and the assignment was made on the basis of expected bond distances around these atoms and by analogy to the assignment of YbGaSn. The bond distances within the layers for Ga–Ge and Ga–Sn are 2.520(2)Å and 2.696(2)Å respectively, indicating strong bonding.

There are four such layers in the unit cell, ordering in an ABCD fashion. The AB and CD layers form respective pairs sandwiching the Yb(1) atoms. Within each pair—AB and CD—the Ga atoms are in alignment (that is, they face each other) so that they present the closest approach between layers in each pair and provide the binding site for the Yb(1) atoms. The Yb(2) atoms are found between the AB and CD pairs and bind to Ge or Sn atoms (Fig. 1a). Yb(1) has a trigonal prismatic coordination of Ga atoms (Fig. 1c), with bond distances of 2.921(2)Å in YbGaGe and 2.966(2)Å in YbGaSn.

This anomalously large difference between the Yb(1)–Ga bond distances in the two compounds was a first indication of the unusual nature of YbGaGe. Yb(2) is coordinated octahedrally by Ge (or Sn) atoms with distances of 3.078(1)Å and 3.238(1)Å respectively (Fig. 1d). Valence bond sum calculations, carried out to assess the assignment of YbGaSn. The bond distances within the layers for Ga–Ge and Ga–Sn are 2.520(2)Å in YbGaGe and 2.696(2)Å in YbGaSn.

Another peculiar characteristic of these two structures that led us to investigate their properties further was the difference in the Ga–Ge distances between adjacent AB and CD layers that surround Yb(1). In YbGaSn this distance is 2.994(1)Å, and is considered short enough for a weak interaction. Despite the presence of the smaller Ge atom in YbGaGe, the Ga–Ge distance is much longer at 3.248(1)Å, and cannot be considered a bonding interaction. This lengthening is the consequence of electron transfer from a formally Yb²⁺ ion to a Ga–Ga bond, resulting in partial oxidation to Yb³⁺ and reductive cleavage of the Ga–Ga bond. The shortened Ga–Yb(1) bond distance is the consequence of electron transfer from a formally Yb²⁺ ion to a Ga–Yb bond, resulting in partial oxidation to Yb³⁺ and reductive cleavage of the Ga–Ga bond. The shortened Ga–Yb(1)

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**Figure 1** Crystal structure details of YbGaGe. **a**, Unit cell of YbGaGe. Red atoms are Ga, blue atoms are Ge and yellow atoms are Yb. The layers A, B, C and D are indicated. **b**, Structure viewed down the c axis of the P6₃/mmc unit cell. **c**, Immediate trigonal prismatic coordination environment of Yb(1). **d**, Octahedral coordination of Yb(2). Atomic coordinates (x₁₀⁴) and equivalent isotropic displacement parameters (Å² × 1₀⁵) for YbGaGe/YbGaSn are as follows, where Ueq is defined as one-third of the trace of the orthogonalized Uij tensor. For Yb(1), (x, y, z) = (0, 0, 2,500) and Ueq = 14(1)/16(1). For Yb(2) (x, y, z) = (0, 0, 0) and Ueq = 10(1)/11(1). For Ge/Sn, (x, y, z) = (3,333, −3,333, 6,128(1)/6,146(1)) and Ueq = 9(1)/12(1). For Ga, (x, y, z) = (3,333, −3,333, 1,531(2)/1,633(2)) and Ueq = 14(1)/14(1).
distance and compressed $c$ axis in the Ge analogue is due to the fact that Yb(1) in YbGaGe has mixed valency, $2+/3+$, and thus has a smaller radius.

There is a certain composition width associated with the phase of YbGaGe. For example, the phase can tolerate a certain deviation from the ideal stoichiometry in the form of YbGa$_{1+x}$Ge$_{1-x}$ (when the material is made from Ga-rich conditions) and YbGa$_{1-x}$Ge$_{1+x}$ (when the material is made from Ge-rich conditions) and this is evident in

Figure 2. Magnetic susceptibility and electrical conductivity data. a) YbGaGe and b) YbGaSn (both $x=1$ and $1/2$). Applied field was 200 Oe for YbGaGe and 500 Oe for YbGaSn. c) Variable-temperature electrical conductivity for YbGaGe. Transport measurements were made using the standard four-probe configuration.

Figure 3. Thermal expansion data. a) Unit-cell volume versus temperature for YbGaGe. b) and c) $a$ and $c$ cell edge lengths versus temperature for YbGaGe. c) Unit-cell volume versus temperature for YbGaSn. Single-crystal measurements were made by collecting a full set of data at room temperature, 200K and 100K. The lowest attainable temperature was 100K. All data sets were collected on the same crystal.
Effective moment is observed (see below). By comparison, YbGaSn shows a very small NTE in YbGaGe (along the a-axis; Table 1) and the overall ZTE derive from the internal electronic charge transfer of the Yb ions in the compound.

YbGaGe is a metallic material, with polycrystalline compaction of it showing room-temperature conductivity of $\sim 2400\,\text{S}\cdot\text{cm}^{-1}$. As seen in Fig. 2c, the conductivity of YbGaGe at 77 K is approximately 3700 $\text{S}\cdot\text{cm}^{-1}$ and decreases to 2200 $\text{S}\cdot\text{cm}^{-1}$ by 400 K. By comparison, the conductivity of ZrW$_2$O$_8$ is $<10^{-8}\,\text{S}\cdot\text{cm}^{-1}$ at 500 K.

The very few materials that exhibit NTE (or ZTE) are insulators and can only be used as ceramics, insulators, or in optics. Thus, there is a need for new materials with similar thermal expansion behaviour over a range of temperatures but that are capable of conducting electric current. YbGaGe combines these characteristics and promises to enable new applications. Furthermore, the electronic, rather than geometric, mechanism operating in YbGaGe may possibly be exploited in the future to design other ZTE or NTE materials through the suitable selection of mixed-valency metal systems and surrounding elements.

Methods

Synthesis of YbGaGe and YbGaSn

The pure phase of YbGaGe (which is stable in air) was obtained by directly combining the elements in their stoichiometric ratios and heating first to 850 °C for 96 h followed by quick cooling to room temperature (−23 °C) over 12 h. YbGaSn was prepared similarly by heating to 700 °C. Elemental analysis performed on several crystals indicate a YbGaSn (or Sn) ratio of 1:1:1, consistent with the X-ray crystallographic analysis. Differential thermal analysis performed on YbGaSn showed no melting or any phase change up to 1000 °C. Samples with excess Ga or excess Ge can be prepared accordingly by adjusting the Yb:Ga:Sn ratio.

X-ray diffraction

Single-crystal X-ray diffraction data for YbGaGe and YbGaSn were collected at 293 K on a Siemens SMART Platform CCD diffractometer. The structure refinements were done with the SHELXTL package of crystallographic programs. Calculations were carried out with Valence Bond Calculator version 2.00 (ref. 14). YbGaSn was used as the standard reference for Yb–Ga bond distances.

For YbGaGe: hexagonal P6$_3$/mmc (no.194), a = 4.2056(8)$\,\text{Å}$, c = 16.780(5)$\,\text{Å}$, Z = 3, V = 257.3(1)$\,\text{Å}^3$, $d_{\text{exp}} = 6.112\,\text{g}\cdot\text{cm}^{-3}$, $\mu = 43.28\,\text{mm}^{-1}$, $2.43\,\% < \theta(\text{MoKα}) < 26.85\,\%$, number of total reflections = 1352, unique reflections = 141 ($R_{\text{int}} = 0.0434$); final R indices for all data, $R_1 = 0.0279$, $wR_2 = 0.074$ for $I > 2\sigma(I)$.

For YbGaSn: hexagonal P6$_3$/mmc (no.194), a = 4.4352(9)$\,\text{Å}$, $c = 17.291(5)$, Z = 3, $V = 294.6(1)$, $d_{\text{exp}} = 6.113\,\text{g}\cdot\text{cm}^{-3}$, $\mu = 36.47\,\text{mm}^{-1}$, $2.43\,\% < \theta(\text{MoKα}) < 26.60\,\%$, total reflections = 1346, unique reflections = 169 ($R_{\text{int}} = 0.046$); final R indices for all data, $R_1 = 0.036$, $wR_2 = 0.092$ for $I > 2\sigma(I)$.

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Reduction of soil carbon formation by tropospheric ozone under increased carbon dioxide levels

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In the Northern Hemisphere, ozone levels in the troposphere have increased by 35 per cent over the past century4, with detrimental impacts on forest2,3 and agricultural1 productivity, even when forest productivity has been stimulated by increased carbon dioxide levels5. In addition to reducing productivity, increased tropospheric ozone levels could alter terrestrial carbon cycling by lowering the quantity and quality of carbon inputs to soils. However, the influence of elevated ozone levels on soil carbon formation and decomposition are unknown. Here we examine the effects of elevated ozone levels on the formation rates of total and decay-resistant acid-insoluble soil carbon under conditions of elevated carbon dioxide levels in experimental aspen (Populus tremuloides) stands and mixed aspen–birch (Betula papyrifera) stands. With ambient concentrations of ozone and carbon dioxide both raised by 50 per cent, we find that the formation rates of total and acid-insoluble soil carbon are reduced by 50 per cent relative to the amounts entering the soil when the forests were exposed to increased carbon dioxide alone. Our results suggest that, in a world with elevated atmospheric carbon dioxide concentrations, global-scale reductions in plant productivity due to elevated ozone levels will also lower soil carbon formation rates significantly.

Table 1 Total carbon and δ13C of soils and the acid-insoluble fraction

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<th>Total soil carbon</th>
<th>Acid-insoluble fraction</th>
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<tbody>
<tr>
<td></td>
<td>Total C (g m⁻²)</td>
<td>δ13C (‰)</td>
</tr>
<tr>
<td>Control</td>
<td>5,385 ± 241</td>
<td>−26.7 ± 0.11</td>
</tr>
<tr>
<td>Elevated O3</td>
<td>5,237 ± 72</td>
<td>−26.9 ± 0.08</td>
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<tr>
<td>Elevated CO2</td>
<td>5,683 ± 480</td>
<td>−28.3 ± 0.10</td>
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<tr>
<td>Elevated O3 + CO2</td>
<td>5,114 ± 289</td>
<td>−27.6 ± 0.10</td>
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Determined for mineral soil from 0 to 20 cm. Values are mean ± s.e.

Figure 1 Total carbon incorporated into soils during 4 yr of exposure to elevated O3 + CO2 and elevated CO2. Values are mean ± 1 s.e.; P < 0.01.

Figure 2 Carbon incorporated into the stable acid-insoluble fraction of soils during 4 yr of exposure to elevated O3 + CO2 and elevated CO2. Values are mean ± 1 s.e.; P < 0.01.

Large areas of the Earth are exposed to concentrations of tropospheric ozone (O3) that exceed levels known to be toxic to plants16. In addition to reducing plant growth, exposure to elevated O3 can also alter plant tissue chemistry7 and reduce allocation of carbon to roots and root exudates8–10. Whereas the effects of O3 on these aspects of plant biology have been widely investigated in chamber studies, examination of these effects on below-ground carbon cycling in intact forests only became possible in 1997 with the establishment of the FACTS-II (forest–atmosphere carbon transfer and storage) FACE (free-air carbon dioxide enrichment) experiment in Rhinelander, Wisconsin, USA. The long-term FACE experiment in Rhinelander examines how plant–plant and plant–microbe interactions may alter ecosystem responses to elevated O3 and carbon dioxide (CO2) through four treatments: control, elevated CO2, elevated O3 and elevated O3 + CO2. In plots where O3 and CO2 are elevated, concentrations were maintained at ~150% of ambient levels11. To examine the effects of atmospheric trace gases on both ecological interactions and on whole-ecosystem carbon cycling, each plot is split to include a pure aspen forest, a mixed aspen–birch forest and a mixed aspen–maple forest. These species were chosen because they are among the most widely distributed trees in northern temperate forests.

Here we compare soil carbon formation in aspen and aspen–birch subplots under elevated CO2 and elevated O3 + CO2 (three plots each) to understand how exposure to O3 under elevated CO2 alters soil carbon formation. We used CO2 derived from fossil fuel with its highly depleted 13C signature to fumigate plant canopies in the elevated CO2 and elevated O3 + CO2 plots. Leaf and root carbon inputs in the elevated CO2 and elevated O3 + CO2 plots had a δ13C signature of approximately −41.6 ± 0.4‰ (mean ± s.e.) in contrast to leaf and root inputs of −27.6 ± 0.3‰ in the control plots. The δ13C signature of soil carbon was −26.7 ± 0.2‰ before fumigation and


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