Ytterbium divalency and lattice disorder in near-zero thermal expansion YbGaGe

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While near-zero thermal expansion (NZTE) in YbGaGe is sensitive to stoichiometry and defect concentration, the NZTE mechanism remains elusive. We present x-ray absorption spectra that show unequivocally that Yb is nearly divalent in YbGaGe and the valence does not change with temperature or with 1% B or 5% C impurities, ruling out a valence-fluctuation mechanism. Moreover, substantial changes occur in the local structure around Yb with B and C inclusion. Together with inelastic neutron scattering measurements, these data indicate a strong tendency for the lattice to disorder, providing a possible explaination for NZTE in YbGaGe.

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Observations of near-zero thermal expansion (NZTE) or negative thermal expansion (NTE) are relatively rare, especially near room temperature. The most famous example is probably invar ($Fe_{64}Ni_{36}$) which has a NZTE volume expansion coefficient $\beta \approx 4 \times 10^{-6}$ K^{-1}. Recently, YbGaGe (Fig. 1) has been identified as a potential NTE and NZTE material,[1] with β in the -1.5×10^{-5} K^{-1} range, depending on the Ga/Ge ratio. In fact, the exact stoichiometry has turned out to be an important factor, with many subsequent measurements unable to reproduce the original work.[2–5] In particular, β is typically between about 2.5×10^{-5} K^{-1} and 4.0×10^{-5} K^{-1}, values that are typical for intermetallics. Understanding the differences between these samples should eventually allow the reproducible fabrication of, what should be, a technologically important material.

A fundamental difference between the original and subsequent measurements is the magnitude and the sign of the magnetic susceptibility. In Ref. 1 a Curie-Weiss-like susceptibility was observed above about 100 K with an effective moment of $\mu_{eff} \approx 4.12\mu_B$, close to the full moment expected from free Yb^{3+} ions (4.54 μ_B). Below 100 K, a sharp decline in the moment occured, with $\mu_{eff} \approx 0.82\mu_B$. These authors pointed out that a bond-valence sum[6] of the valence for each of the two ytterbium sites (Fig. 1) gives a valence of +2.6 for the Yb(1) site and +2.0 for the Yb(2) site. Such a result is consistent with a mixed valent state for at least one of the Yb sites. Together with the magnetic susceptibility data, this observation lead the authors to conclude that the mechanism for the observed NTE was a change in the Yb valence with temperature toward a divalent state below 100 K, consistent with the susceptibility.

In direct contrast to those first measurements, subsequent measurements find a diamagnetic susceptibility for the pure compound,[2–5] even over a wide rage of the Ga/Ge occupancy ratio[4] and with other defects.[5] These susceptibility measurements are a very strong indication of divalent Yb at all measured temperatures. However, if the real Yb valence is +2.6 or even less, this could be an indication of a very high Kondo temperature, T_K, perhaps well in excess of 1000 K. Given this possibility and the fact that the magnetic susceptibility is expected to go to a constant $\chi_0 \propto 1/T_K$ at temperatures below T_K, the diamagnetic contribution from the nonmagnetic matrix needs to be carefully considered before declaring that all the Yb is divalent. A spectroscopic measurement of the Yb valence would provide a direct measurement.

As an alternative to the valence-instability model for the thermal expansion behavior in this system, Drymiotis et al.[5] considered the possibility that this behavior could be driven by disorder. They note that the original synthesis was performed in graphite crucibles and therefore grew YbGaGe with small amounts of carbon and boron in alumina crucibles. They found that the thermal expansion could be reduced by about 50% with only 0.5% carbon or boron included in the starting materials. They conjecture that, although they did not obtain NTE and still observe diamagnetic behavior, that the mechanism for NTE in Ref. 1 has a similar origin.

Here, we report x-ray absorption near-edge structure (XANES) measurements at the Yb L_{III} edge that show ytterbium in these materials is, in fact, nearly divalent, that the valence does not change dramatically with carbon or boron doping, and that the remaining trivalent component is easily explained as due to an impurity
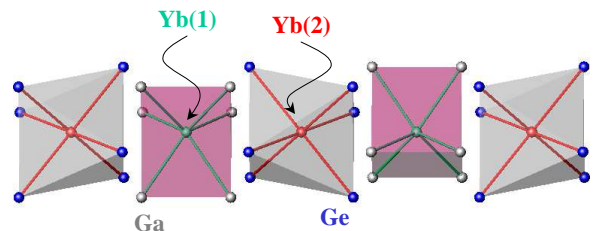

FIG. 1: Stacking of the Yb(1)-Ga$_6$ trigonal prisms and the Yb(2)-Ge$_6$ octahedra in the $P6_3/mmc$ hexagonal cell.
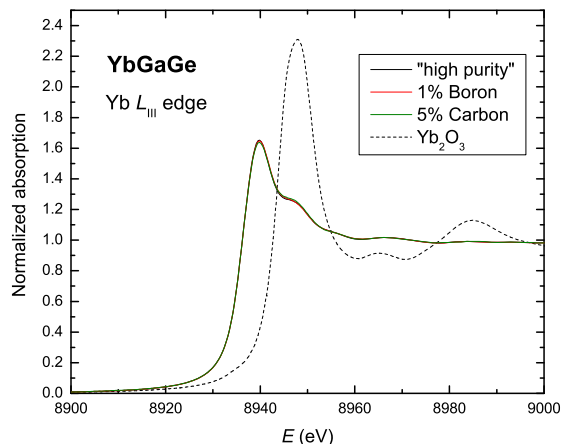
FIG. 2: Yb L_{III}-edge XANES spectra for the pure, 1% B, and the 5% C samples of YbGaGe, all collected at 30 K, together with a room-temperature spectrum of Yb_2O_3. The three YbGaGe spectra are nearly identical, and are therefore difficult to discern in this figure.

phase (for example, Yb_2O_3 or a Yb-Ga binary alloy). In addition, extended x-ray absorption fine-structure (EX-AFS) measurements of the local structure environment around the Yb atoms shows that small amounts of carbon or boron in YbGaGe have a surprisingly large effect on the average local structure. This extreme sensitivity to interstitials appears to be the root cause of near-zero thermal expansion in this system.

Samples were prepared as in Ref. 5. For the present work, in addition to a high purity sample grown in an yttria crucible, carbon and boron doped samples were also fabricated, one with nominally 1% boron and another with 5% carbon. X-ray diffraction measurements indicate the YPtAs structure type in the hexagonal $P6_3/mmc$ space group, with small ($<5\%$) unidentified impurity phases. The thermal expansion coefficients for the yttria grown sample is 3.19×10^{-5} K^{-1}. The thermal expansion for the 1%B and 5%C samples is expected to be less than for the 0.5%B sample[5] ($\beta = 1.70 \times 10^{-5}$ K^{-1}). Preliminary data taken on the 1% B sample, using a thermal expansion cell, confirmed our expectation. Magnetic susceptibility measurements indicate diamagnetic behavior with a small impurity tail corresponding to free Yb^{3+} moments. The effective moment per mole, calculated from the impurity tail (Ref. 5) varied between 0.05 and 0.23 μ_B and showed no correlation with B or C concentration.

The XANES data were collected on Beamline 10-2 at the Stanford Synchrotron Radiation Laboratory. The samples were first re-ground, passed through a 20 μm sieve, brushed onto adhesive tape, and stacked to achieve an absorption length change at the Yb L_{III} edge (8.944 eV) of $\Delta \mu t \approx 1$. Data were collected in transmission mode with a defocused beam from a half-tuned Si(220) double-crystal monochromator resulting in an energy resolution of about 2.0 eV. Since the core-hole lifetime is

about 4.2 eV, the reported spectra are not lifetime limited. All spectra were collected under the same conditions. After preparing the samples, they were placed in a LHe flow cryostat, and data were collected between 30 and 300 K. Data were reduced and fit using standard procedures.[7] In particular, the absorption from the Yb L_{III} edge as a function of the incident energy E, $\mu_a(E)$, was isolated from the total absorption $\mu(E)$ after approximating all other contributions by extrapolating from the pre-edge data and forcing $\mu_a(E)$ above the edge to follow a Victoreen formula.[7] The EXAFS oscillations were isolated by fitting a 7-knot cubic spline to approximate the embedded-atom absorption $\mu_0(E)$, resulting in the EXAFS function $\chi(k) = (\mu_a(k) - \mu_0(k))/\mu_0(k)$, where k is the photoelectron wave vector obtained from E and the threshold energy E_0, arbitrarily taken as the energy at the half-height of the edge. The oscillations in $\chi(k)$ are due to interference of the backscattered and outgoing parts of the photoelectron wave function modulating the absorption coefficient, and as such, a Fourier transform (FT) of $\chi(k)$ produces peaks in r-space corresponding to scattering shells around the absorbing atomic species. Note that phase shifts of the outgoing and back scattered photoelectron make the FT more complicated than a true radial distribution function, so detailed fits using the RSXAP package[7–9] and theoretical lineshapes calculated by FEFF7[10] were performed to extract the local structure information.

The XANES results are displayed in Fig. 2, together with the spectra of Yb_2O_3 as a trivalent Yb reference. The main peak ("white line") position of the Yb_2O_3 reference is typical of trivalent Yb, including in intermetallic compounds. There is a clear energy shift of about 8 eV between the YbGaGe compounds and the reference, indicating Yb in these intermetallics is predominantly divalent. In addition, we observe a small bump at the same position as the white line in Yb_2O_3, indicating a small trivalent component. By fitting these features to a pseudo-Voigt function each for the divalent and the trivalent resonances and an integrated pseudo-Voigt to model the edge step, we have found that one can extract the f-hole occupancy n_f within about 5% compared to other Yb intermetallics we have studied.[11,12] For these data, we obtain $n_f = 0.17 \pm 0.10$. The small trivalent component could be due to an intermediate valent ground state in YbGaGe, but is more likely due to intermetallic or oxide impurities, as will be demonstrated below. As is clear in Fig. 2, there is very little difference in the f-occupancy between the three samples. Moreover, there is very little change in n_f with temperature, much less than 1% between 30 and 300 K.

The EXAFS data and fit for the pure YbGaGe sample are shown in Fig. 3. The data quality is very high and the r-space fit quality is also very good above about 2 Å. However, below 2 Å, there is some unexplained amplitude, as reflected in the reported $R(\%) = 13.1$ (a high-quality EXAFS fit should be near 5%). Some of this amplitude can be explained with between 5-10% Yb_2O_3.
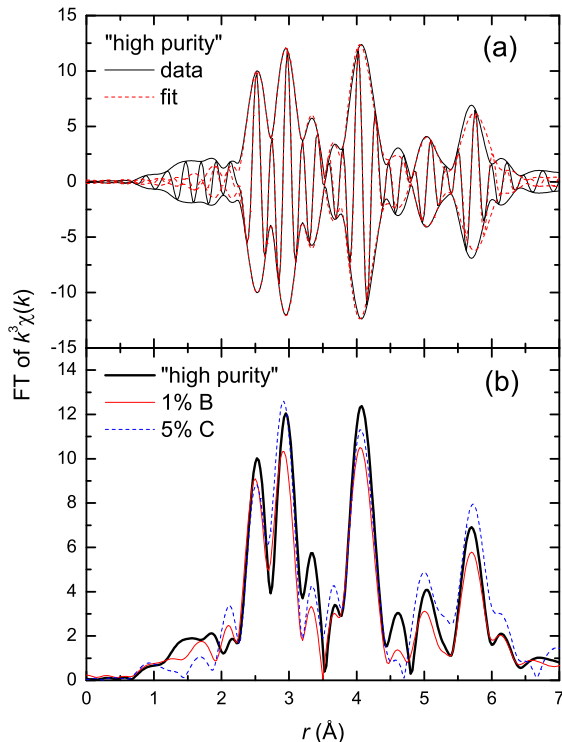
FIG. 3: EXAFS data in r-space for (a) the pure YbGaGe sample, and (b) all three samples at 30 K. The Fourier transforms (FT) are between 2.5 and 16.0 Å^{-1}, Gaussian narrowed by 0.3 Å^{-1}. The fit in (a) is between 1.2 and 6.0 Å and the outer envelope is $\pm$ the amplitude, and the modulating inner line gives the real part of the complex transform. Only the amplitude is shown in (b).

Even so, the fit shown in Fig. 3(a) already includes such an impurity, so there is likely some other kind of impurity present, possibly in addition to the sesquioxide. We have tried other intermetallic phases such as YbGa and YbGa$_2$ with only moderate success. In any case, the fit parameters are very close to the expected values from bulk diffraction studies, and the variance of the pair-distance distribution widths (Debye-Waller factors), σ^2, are also all of a reasonable magnitude.

The r-space transforms for all three samples at 30 K are shown in Fig. 3(b). There are very clear differences between the pure and the substituted samples at all length scales. The fit results for the substituted samples are similar to the pure case with the following exceptions: (1) the bond lengths are very similar except for the Yb(1)-Ge pair in the 1% boron substituted sample, nominally at 3.35 Å, but instead at 3.13 Å; (2) many of the Debye-Waller factors are substantially different; and (3) the amplitude reduction factor S_0^2 is unphysically small, ≈ 0.5-0.6 in both cases. These results point strongly to the presence of multiple phases over and above that observed for the pure YbGaGe sample. For instance, the short value for the Yb(1)-Ge pair may be indicative of a YbGa-like phase.[13] More directly, the reduction in S_0^2
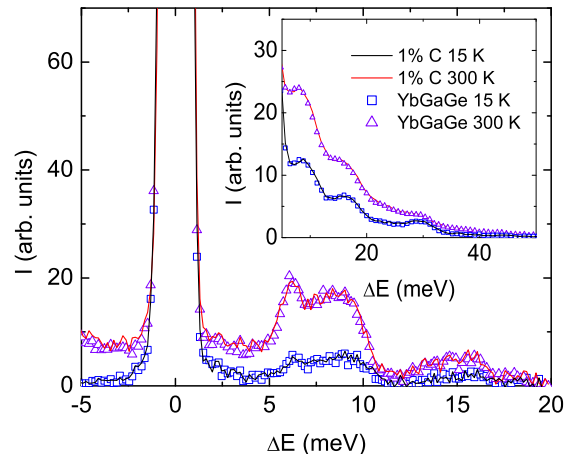

FIG. 4: Neutron scattering intensity versus energy transfer ΔE at 15 K and 300 K for undoped and C-doped YbGaGe. The incident energy in the main panel was 25 meV, and 125 meV in the inset.

(an overall scale factor) and the variations in the Debye-Waller factors, while still allowing for a high quality fit, can be explained by allowing for nearly amorphous or high distorted regions of the sample. The presence of such a high fraction of the sample being so disordered (about 20%) indicates that the presence of boron or carbon in the lattice has relatively long-range effects on the local structure.

In order to determine whether these changes are vibrational in origin, we performed inelastic neutron scattering measurements on polycrystalline samples of YbGaGe, both undoped and doped with 1% carbon. The measurements were performed on the PHAROS time-of-flight spectrometer at the Manuel Lujan Los Alamos Neutron Science Center (LANSCE). We used incident energies of 25 and 125 meV and we measured at three temperatures, 15, 78 and 300 K. (The 78 K data are not show in Fig. 4 for clarity.) We summed groups of detectors to improve statistics. The data in Fig. 4 are from detectors with an average scattering angle of $= 89°$; for such large scattering angles, the spectrum of a polycrystalline sample approximates the phonon density-of-states. Peaks are observed near 6, 8.5, 16 and 30 meV. The fact that the phonon spectra for both pure and carbon-doped YbGaGe samples are identical means that the changes in the thermal expansion and the XAFS that occur in the C-doped samples cannot arise from a bulk distortion of the lattice, since this should affect the phonon frequencies. Instead, these changes must be due to random or near-random disorder. Presumably, this disorder reduces the anharmonicity in the pair potentials that generate the thermal expansion. Apparently, these neutron measurements are not sensitive to such an effect. Moreover, fits to the EXAFS including an anharmonic term, that is, a third cumulant,[14] are inconclusive.

These results strongly support the conclusion by

Drymiotis *et al.*[5] that the mechanism for the reduced thermal expansion, and possibly for the NTE observed by Salvador *et al.*,[1] is carbon defects. It also confirms the conclusions drawn by several researchers[2–5] that the diamagnetic susceptibility is indicative of a divalent Yb state at all measured temperatures.

Unexplained facts remain regarding the original Salvador *et al.*[1] work. First, no subsequent published measurement has produced a magnetic susceptibility consistent with mostly Yb^{3+} above 100 K. This discrepancy may be due to the exact impurities that may have been present in the original samples. However, given the magnitude of the susceptibility, it seems unlikely that an impurity could generate a susceptibility corresponding to bulk Yb^{3+} at room temperature. Given this structure's propensity to disorder with small defect concentrations, the possibility remains that the original samples did, in fact, undergo a valence change upon cooling.

Another peculiar fact is that the bond-valence sums give a much higher valence to the Yb(1) site ($+2.6$) than the Yb(2) site ($+2.0$). This analysis depends on the z-parameter for the Ga and Ge sites, a quantity that has not been re-measured. The EXAFS results reported here are similarly insensitive to the differences between the Ga and Ge atoms as the x-ray diffraction measurements; however, the results are consistent with two separate Yb sites with different coordination environments, as expected from the diffraction measurements. Indeed, the local measured bond lengths are all consistent with those expected from the diffraction results and their associated z-parameters. The bond-valence sum conclusion also depends on the relative mixture of Ge and Ga on their nominal sites, a quantity that is essentially assumed both by the diffraction and the EXAFS measurement.

In conclusion, the f-hole occupancy n_f has been measured in YbGaGe using Yb L_{III}-edge XANES spectroscopy, and apart from a small trivalent component that is likely due to oxide or intermetallic impurities, Yb in this system appears to be divalent, consistent with several previous measurements, such as magnetic susceptibility.[2–5] The valence does not change dramatically either with temperature or with small amounts of boron or carbon substitution. Although the local structure obtained by fitting the EXAFS is consistent with that expected from the bulk crystal structure, systematic differences with the fitting model indicate the presence of some other phase, especially in the substituted materials. In particular, the 1% boron and 5% carbon substituted samples show large differences in the EXAFS compared to the pure sample, indicating a very large effect on the local lattice for such small amounts of impurities. The inferred presence of such highly disorded regions is consistent with the conclusion reached in Ref. 5 that the reduction of the thermal expansion is related to defects caused by chemical substitution.

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