Anisotropic distortions in Sb doped CePt$_4$Ge$_{12}$

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Abstract.

We investigated the local structure of the Sb doped skutterudite CePt$_4$Ge$_{12-x}$Sb$_x$ using the Extended X-ray Absorption Fine Structure Technique (EXAFS). As the concentration of Sb is increased the disorder around Ce increases rapidly, and for $x = 3$, the peak for the nearest neighbor (Ce-Ge) is no longer observed. In contrast, for the Pt site, the disorder of the nearest neighbors is small even for $x = 3$. Thus the distortions are anisotropic and appear to be mainly in the plane of the Ce-Ge bonds and Ge$_4$ rings. The increased disorder about Ce will decrease the lattice thermal conductivity at low temperatures, and likely is part of the reason for improved thermoelectric properties for the $x = 1$ sample.

1. Introduction

The filled skutterudites LnX$_4$T$_{12}$ (Ln = rare earth; X = Fe, Ru, Os, Pt; T = P, As, Sb, Ge) are a broad class of materials with several unusual properties[1], including a low thermal conductivity, κ, and a high Seebeck coefficient, both of which are important for thermoelectric applications. The compound CePt$_4$Ge$_{12}$, has only recently been synthesized[2, 3, 4, 5] and no local structure studies have been reported. For this material (space group $Im\bar{3}$), twenty-seven Pt atoms form a cubic unit cell composed of eight smaller cubic cages. Six of these cages contain square rings of four Ge atoms, while the other two cages enclose Ce atoms. The Ln atoms in other skutterudites exhibit “rattling” behavior, with large amplitude vibrations and the ability to scatter phonons effectively, which contribute to the low value of thermal conductivity. Interestingly, substituting Sb for Ge greatly enhances the thermoelectric properties of the material[3]. Here we use the Extended X-ray Absorption Fine Structure (EXAFS) technique to probe the local structure in CePt$_4$Ge$_{12-x}$Sb$_x$; in particular, we investigate the rattling behavior of Ce and observe how the local structure varies with Sb doping[4].

2. Experimental Details

EXAFS samples were prepared by grinding polycrystalline samples, prepared as in Ref. [5], into a powder, which was then filtered through a mesh sieve to produce a sufficiently fine grain. The fine powder was brushed onto scotch tape in a single layer; two pieces were pressed together to fully enclose the powder sample. These double layers were cut into strips and stacked together to achieve an absorption step height in the range 0.3 to 0.7 for the edge being studied.
EXAFS data were collected on beamlines 4-1 and 7-3 at the Stanford Synchrotron Radiation Lightsource (SSRL) using Si 220 monochromator crystals. The monochromator was detuned 50% to minimize harmonics. EXAFS transmission data at the Pt $L_{III}$, Ge $K$, and Sb $K$ edges and fluorescence data for the Ce $L_{III}$ edge were collected as a function of temperature $T$ (5-300 K). EXAFS data reduction and analysis were carried out using the RSXAP package[6].

3. EXAFS Data

![Figure 1](image-url)  
*Figure 1. $r$-space data for a) the Ce $L_{III}$, b) the Pt $L_{III}$, and c) Ge $K$ edge, at 8 (blue), 150 (green), and 300 K (red), for $x = 0$ (top), 1 (middle), and 3 (bottom). FFT ranges are 2.8-9.5, 3-14.7, and 2.9-9.7 Å for Ce, Pt, and Ge respectively.*

In Figure 1 we plot the $r$-space data as a function of $T$ for the Ce $L_{III}$, Pt $L_{III}$, and Ge $K$ edges respectively for $x = 0$, 1, and 3. Peaks in EXAFS data are always shifted to lower $r$ compared to actual distances from crystallographic data. For the Ce data, the first peak near 2.9 Å is a composite of the Ce-Ge peak (12 Ge neighbors at 3.32 Å) and a weaker Ce-Pt peak near 3.4 Å (8 Pt neighbors at 3.7 Å) that overlaps the Ce-Ge pair. The data for $x = 0$ or 1 show a large amplitude at 8 K and a very strong $T$-dependence, which is characteristic of a rattler atom. However, as more Sb is substituted, the amplitude is drastically reduced, with no clear peak or $T$-dependence observed for $x = 3$; the $k$-space data above 150 K have a low amplitude and are too noisy to reduce. Thus the environment about Ce is highly disordered even at 5 K.

For the Pt data, the first peak (2.2 Å) is a Pt-Ge pair at 2.48 Å. The group of peaks from about 3.2 to 4.5 Å is a composite of a second Pt-Ge pair at 4.14 Å, a Pt-Pt pair at 4.31 Å, as
well as the weak Pt-Ce pair at 3.73 Å. The Pt data show a weaker temperature dependence, as the amplitude at 300 K is only diminished by about 35%. The data are also less affected by the doping level; even for $x = 3$, the amplitude of the first peak (Pt-Ge) at low-T is only reduced by 25%. However, the further neighbor peaks are no longer visible indicating significant distortion within a unit cell.

For the Ge data, the first (double) peak (1.8-3.5 Å) is the sum of two interfering pairs, Ge-Pt ($r = 2.48$ Å) and Ge-Ge ($r = 2.56$ Å). The second main peak from about 3.5 to 5 Å is composed of a Ge-Ge neighbor at 3.26 Å, a small Ge-Ce at 3.32 Å, and two more unresolved Ge-Ge pairs (3.62 and 3.75 Å respectively). The amplitude drops by about 50% for $x = 3$, making it more disordered than the Pt data, but less than the Ce data. An interesting phenomena is that at high doping levels, the amplitude at 2.1 Å changes little while that near 3 Å is sharply reduced, suggesting that the Ge-Ge peak disorders faster with doping than the Ge-Pt peak. Also, the interference dip at 2.4 Å disappears - from the changing interference between the first two pairs.

4. Analysis
The r-space data were fit to a sum of theoretical EXAFS functions calculated using the program FEFF8[7] and the known structure, taken from diffraction data[2]. For Ce, two peaks were fit (Ce-Ge and Ce-Pt) and the ratio of the number of neighbors was constrained to the known coordinations from diffraction data. From such fits, the pair distance and broadening, $\sigma$, were extracted for each pair distribution function. An example of a fit for the 8 K Ce data is shown in Figure 2 (Fit ranges: 2.0-4.4 Å for Ce data and 1.9-4.2 Å for Pt data).

From fits at multiple temperatures, $\sigma^2(T)$ was extracted for two neighbors in the Ce data and three neighbors in the Pt data at $x = 0$ and 1. These are plotted in Figure 3a,b respectively. For the nearest neighbor pair, Ce-Ge, at $x = 0$, $\sigma^2(T)$ follows an Einstein model well (rigid cage approximation), with a low static off-set. The $x = 1$ sample shows a higher degree of disorder, and a much larger value of $\sigma^2_{static}$. The Ce-Pt pair has a significant static contribution even at $x = 0$, and at $x = 1$ the data are too disordered to fit using an Einstein model.

The Pt $\sigma^2(T)$ data are better described using a correlated-Debye model. Good fits are obtained for the Pt-Ge and Pt-Pt pairs, for $x = 0$ and 1. However, the $x = 1$ sample has a higher static offset than the undoped material.

5. Conclusions
The Einstein temperature for the nearest neighbor Ce-Ge pairs is low, consistent with rattler behavior for rare earth atoms in other skutterudites. In addition, this pair is quite well ordered at low T for $x = 0$; i.e., $\sigma^2_{static}$ is small. With increasing Sb doping levels, the Ce $L_{III}$ edge data rapidly becomes disordered ($\sigma^2_{static}$ increases dramatically) and at $x = 3$, the Ce-Ge peak
is no longer well defined. Even at \( x = 1 \), the second neighbor Ce-Pt pair is too disordered to be fit to an Einstein model. In contrast, the Pt-Ge peak is only slightly distorted even at \( x = 3 \). The environment about Ge is in between; more disordered than around the Pt site but less than about the Ce site. This suggests that the distortions are primarily in the plane of the Ge\(_4\) rings, mainly towards the rattler atom, Ce. One possibility is that the presence of the dopant pushes some Ce atoms off-center but that requires further investigation. The increased disorder will decrease the lattice thermal conductivity and likely plays a role in the improvement of thermoelectric properties for the Sb doped materials.

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