Chapter 6

**XAFS ANALYSIS OF PURE AG AND AU**

The temperature dependence of the near-neighbor XAFS for pure Ag and pure Au will be analyzed in this chapter. After demonstrating that FEFF calculations can reasonably represent the full multiple scattering XAFS through the fourth shell for low temperature data of pure Ag, the FEFF calculations will be taken as a reliable enough theory to use in the analysis of the first shell at all temperatures. The expressions for the cumulants from the one-dimensional anharmonic potential presented in chapter 5 will be used to model the XAFS in the high-temperature limit. The results for the anharmonic force constants found from these analyses will be used to evaluate the thermodynamic properties of the bonds, and will be compared with values found by more traditional thermodynamic methods. The presentation will be fairly complete for the pure systems, as they will serve as models of the analyses for the impurity-host systems in chapters 8 and 9, where many more results will be presented more concisely.

6.1 The XAFS of Pure Ag

A sample of pure Ag for transmission XAFS was made by mechanically rolling a piece of 99.999% pure Ag shot supplied by United Mineral and Chemical Corp. to 25μm. This thickness gave a total μx of 1.4 and an edge jump of Δμx of 1.2 at the Ag K-edge, at 25514 eV. XAFS measurements were made on this Ag sample by the transmission method at beamline X-11A of the NSLS using a Si (311) double-crystal. To suppress harmonics, the double-crystal monochromator was detuned so as to pass ~ 80% of the maximum intensity of the incident beam. The value of Δμx ≈ 1.2 was confirmed by direct observation of the edge step. The sample was measured at temperatures of 80, 180, 240, 300, 400, 500, 600, 700 and 800 K, with sample temperatures maintained to within 3 K of the nominal values. More details of experimental procedures for making samples, measuring μx, and controlling the temperature are given in chapter 3.

Figure 6.1 shows the measured absorption spectra of Ag at 80K and the back-
Figure 6.1: Measured x-ray absorption spectra for Ag at 80K (solid) and the smooth background (dashed) found by AUTOBK. $R_{\text{bkg}} = 1.60 \, \text{Å}$ was used for all background-removals of pure Ag. Leakage from the first shell was modeled by a FEFF calculation for pure Ag.

ground spline put through this data to isolate the structural $\chi(k)$. The background absorption was found for all signals using AUTOBK with $R_{\text{bkg}} = 1.60 \, \text{Å}$. Data was collected only to $k_{\text{max}} = 13.50 \, \text{Å}^{-1}$, even for low-temperatures, so that there were 13 knots in the background spline, as calculated using Eq. (4.11). A model spectra for the XAFS from FEFF was used to model the leakage of the first shell to $R$ below $R_{\text{bkg}}$.

6.2 Multiple Scattering Analysis of Ag at 80K

As for the pure Cu example of chapter 4, there is sufficient information in the XAFS data of pure Ag that it can be analyzed through the fourth-neighbor distance. In order to indicate the confidence level when using theoretical calculations for XAFS analysis on pure Ag, I will present the multiple-scattering analysis of pure Ag at 80 K. As expected from the analysis of pure Cu, multiple scattering contributions to the XAFS become quite important at distances past the first neighbor, and dominate the signal at the fourth shell, where focused multiple scattering occurs.

The analysis of the Ag XAFS began with a FEFF calculation using only the atomic species, the fcc crystal structure, and a lattice constant of 4.07Å(at 80 K). Setting
Table 6.1: Scattering paths for Ag out to twice the near-neighbor distance from FEFF used in the multiple scattering analysis. Paths indices are listed with half-path-length $R_{\text{eff}}$, degeneracy $N_{\text{degen}}$, number of path legs $N_{\text{leg}} (= N_{\text{scatt}} + 1)$, and Zabinsky curved-wave importance factor $C_{\text{cw}}$.

<table>
<thead>
<tr>
<th>Path Index</th>
<th>$R_{\text{eff}}$ (Å)</th>
<th>$N_{\text{degen}}$</th>
<th>$N_{\text{leg}}$</th>
<th>$C_{\text{cw}}$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.878</td>
<td>12</td>
<td>2</td>
<td>100.0</td>
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<tr>
<td>2</td>
<td>4.070</td>
<td>6</td>
<td>2</td>
<td>18.5</td>
</tr>
<tr>
<td>3</td>
<td>4.317</td>
<td>48</td>
<td>3</td>
<td>7.3</td>
</tr>
<tr>
<td>4</td>
<td>4.913</td>
<td>48</td>
<td>3</td>
<td>3.6</td>
</tr>
<tr>
<td>5</td>
<td>4.985</td>
<td>24</td>
<td>2</td>
<td>38.8</td>
</tr>
<tr>
<td>6</td>
<td>5.370</td>
<td>48</td>
<td>3</td>
<td>4.2</td>
</tr>
<tr>
<td>7</td>
<td>5.370</td>
<td>96</td>
<td>3</td>
<td>12.4</td>
</tr>
<tr>
<td>8</td>
<td>5.756</td>
<td>12</td>
<td>2</td>
<td>12.0</td>
</tr>
<tr>
<td>9</td>
<td>5.756</td>
<td>12</td>
<td>3</td>
<td>4.7</td>
</tr>
<tr>
<td>10</td>
<td>5.756</td>
<td>24</td>
<td>3</td>
<td>45.4</td>
</tr>
<tr>
<td>11</td>
<td>5.756</td>
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<td>4</td>
<td>7.7</td>
</tr>
<tr>
<td>12</td>
<td>5.756</td>
<td>12</td>
<td>4</td>
<td>45.1</td>
</tr>
</tbody>
</table>

The Zabinsky curved-wave importance factors $C_{\text{cw}}$ [76] to 2.5% gives twelve scattering paths out to twice the near-neighbor distance. (These twelve most important paths for Ag are geometrically equivalent to the twelve important paths for Cu found in chapter 4). Table 6.1 lists these twelve scattering paths, their half-path-length, degeneracy, number of scattering legs (which is one more than the number of scattering sites), and Zabinsky curved-wave importance factor (as a percentage of that of the first path). Decreasing $C_{\text{cw}}$ to 1% or even to 0% does not significantly change the fit results or the goodness-of-fit parameters, so only the twelve most important paths will be used in this analysis.

The 80-K Ag data was fit in $R$-space using Fourier transform parameters $w = 2$, $k_{\text{min}} = 2.5$ Å$^{-1}$, $k_{\text{max}} = 13.5$ Å$^{-1}$, and $dk = 1.5$ Å$^{-1}$. The fit with the twelve paths listed in Table 6.1 was done between $R_{\text{min}} = 1.70$ Å and $R_{\text{max}} = 5.50$ Å. There are 26 independent points in this data range for the structural data, and 13 independent points below $R_{\text{min}}$. Following the discussion of section 4.5.3, the independent points below $R_{\text{min}}$ are used to improve the background spline and to check the correlation
Figure 6.2: XAFS $\chi(R)$ for Ag at 80K. The dashed curve shows experimental data; the solid curve shows a fit to the experimental data using multiple-scattering XAFS calculations from FEFF. Four variables were adjusted in the fit: $S_0^2$, $\Delta E_0$, $\alpha$, and $\theta_D$. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.2.

of the background with the structural parameters. Two slightly different fits to the structural portion of the data will be shown.

Four adjustable parameters were used for the structural region in the preliminary fit. A single $S_0^2$ and a single $\Delta E_0$ were used for all paths, and each of these values was varied in the fit. A lattice expansion factor, $\alpha$, giving a value of $\Delta R_j = \alpha R_{\text{eff},j}$ for the distance change for the $j$th scattering path, was also varied. This parameterized $\alpha$ compensated for using a lattice constant of Ag in the FEFF calculation that may have been slightly too large for the 80-K data. The values of $\sigma^2$ for all paths were determined by the Correlated Debye Model [99, 36] which evaluates $\sigma^2$ given the temperature, Debye temperature, and path geometry of a scattering path. A single Debye temperature $\theta_D$ was varied in the fit. Thirteen variables describing the background spline were also varied in the fit to improve the $R$-region below 1.70 Å. Figure 6.2 shows the resulting fit from such a simple model and Table 6.2 lists of the best-fit values, estimated uncertainties, and goodness-of-fit parameters for this fit. The large uncertainties in $S_0^2$ and $\theta_D$ (and, by extension of $\sigma^1$), which are on the order of 10% of the parameter value, reflect the large correlation between these two variables, which was $C(S_0^2, \theta_D) \approx -0.92$. This interdependence of the amplitude parameters shows
Table 6.2: Results of simple fit to 80-K Ag data. Variables adjusted in the fit were $S_0^2$, $\Delta E_0$, $\alpha$, and $\theta_D$, as further discussed in the text. The values and uncertainties reported for $\sigma^2$ were derived from $\theta_D$ and its uncertainty. The $\sigma^2$ for paths 8, 9, 10, 11, and 12 are equivalent in the Correlated Debye Model. Definitions of goodness-of-fit parameters are given in chapter 4. This fit is shown with the data in Fig 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
<td>22.</td>
<td></td>
<td>degrees of freedom</td>
</tr>
<tr>
<td>$\epsilon_R$</td>
<td>0.0173</td>
<td>$\text{A}^{-3}$</td>
<td>uncertainty in $\tilde{\chi}_{\text{data}}(R)$</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>90.6</td>
<td></td>
<td>goodness-of-fit</td>
</tr>
<tr>
<td>$R$</td>
<td>0.0203</td>
<td></td>
<td>goodness-of-fit</td>
</tr>
<tr>
<td>$S_0^2$</td>
<td>0.92(08)</td>
<td></td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\Delta E_0$</td>
<td>$-4.92(60)$</td>
<td>eV</td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$-0.0011(10)$</td>
<td></td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\theta_D$</td>
<td>226.1(16.)</td>
<td>K</td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\sigma_1^2$</td>
<td>0.0035(4)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma_2^2$</td>
<td>0.0043(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma_3^2$</td>
<td>0.0040(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma_4^2$</td>
<td>0.0044(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
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<tr>
<td>$\sigma_5^2$</td>
<td>0.0044(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma_6^2 = \sigma_7^2$</td>
<td>0.0045(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma_8^2 = \cdots = \sigma_{12}^2$</td>
<td>0.0044(5)</td>
<td>$\text{A}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
</tbody>
</table>

that a single temperature is insufficient to determine both $S_0^2$ and $\theta_D$ precisely. This topic will be revisited in the next section, where temperature-dependent data will be used to better determine $S_0^2$.

The background parameters in this simple fit were all quite small. Only one background spline coefficient was reliably non-zero (i.e., had a value larger than its estimated uncertainty), indicating that the original AUTOBK background was adequate. An equally important result is that the largest correlation (in magnitude) between a background and structural variable was $-0.37$ (between a background-spline coefficient near the $R_{\text{bkg}}$ and $\alpha$). This correlation is small enough to conclude that the background does not greatly influence the structural parameters, and that
Figure 6.3: XAFS $\tilde{\chi}(R)$ for Ag at 80K. The dashed curve shows experimental data; the solid curve shows a fit to the experimental data using multiple-scattering XAFS calculations from FEFF. Five variables were adjusted in the fit: $S_0^2$, $\Delta E_0$, $\alpha$, $\sigma^2_1$ (for the first path), and $\theta_D$ (to give $\sigma^2$ for all higher paths). $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.3.

The background is sufficiently well-separated from the XAFS structural information. (A better check of these claims might be to use an intentionally poor background removal in AUTOBK, say with $R_{\text{bkg}} = 0.5 \, \text{Å}$, and then measure the correlation between structural and the background parameters below a more reasonable $R_{\text{bkg}} = 1.7 \, \text{Å}$. This is easily done, and does not appreciably change the results for the structural parameters or for the correlations between structural and background parameters.)

Although the fit in Fig. 6.2 looks quite good, closer inspection shows that the amplitudes for the higher shells are not fit as well as that of the first shell. The quality of fit might be improved if the mean-square-displacements disorder parameters for the higher shells were fit separately from that for the first shell. But having twelve different values of $\sigma^2_1$ seems excessive, and probably unnecessary — the fit isn’t that bad. So, as a simple extension, I’ll fit $\sigma^2$ for the first path separately, and constrain the $\sigma^2$ values for all higher shells to be given by the Correlated Debye Model. This adds only one more variable to the fit, and will give a good example of how to decide if the addition of a particular variable is worthwhile.

The resulting fit (with 5 variables for the 26 independent points in the structural
Table 6.3: Results of second fit to 80-K Ag data. Variables adjusted in the fit were $S^2_0$, $\Delta E_0$, $\alpha$, $\sigma^2$ for the first path and $\theta_D$. The values and uncertainties reported for $\sigma^2$ of the higher paths were derived from $\theta_D$ and its uncertainty. This fit is shown with the data in Fig 6.3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$</td>
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<td></td>
<td>degrees of freedom</td>
</tr>
<tr>
<td>$\epsilon_R$</td>
<td>0.0173</td>
<td>$\text{Å}^{-3}$</td>
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</tr>
<tr>
<td>$\chi^2_\nu$</td>
<td>51.3</td>
<td></td>
<td>goodness-of-fit</td>
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<tr>
<td>$\mathcal{R}$</td>
<td>0.0110</td>
<td></td>
<td>goodness-of-fit</td>
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<td>$\Delta E_0$</td>
<td>-4.98(46)</td>
<td>eV</td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>-0.0012(7)</td>
<td></td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\theta_D$</td>
<td>196.(12.)</td>
<td>K</td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\sigma^2_1$</td>
<td>0.0039(3)</td>
<td>$\text{Å}^2$</td>
<td>fitted variable</td>
</tr>
<tr>
<td>$\sigma^2_2$</td>
<td>0.0054(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma^2_3$</td>
<td>0.0049(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma^2_4$</td>
<td>0.0055(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma^2_5$</td>
<td>0.0056(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma^2_6 = \sigma^2_7$</td>
<td>0.0056(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
<tr>
<td>$\sigma^2_8 = \cdots = \sigma^2_{12}$</td>
<td>0.0056(5)</td>
<td>$\text{Å}^2$</td>
<td>derived from $\theta_D$</td>
</tr>
</tbody>
</table>

The second fit is better than the first. This judgment is based on the fact that $\chi^2_\nu$ and $\mathcal{R}$ are cut nearly in half by the addition of one variable. The added $\sigma^2$ is therefore quite important in improving the fit. This suggests that the Correlated Debye Model does only a fair job for pure Ag, and may not be adequate for a careful analysis of multiple-scattering paths, even for close-packed metals. Still, it gives a very good and convenient initial estimate of unknown values of $\sigma^2$. Refinements such as including the effect of angular deviations to $\sigma^2$, might improve the effectiveness of
this model.

The ability of FEFF calculations to be used reliably in XAFS data analysis has been well-established [59, 77, 78] and the fact that good fits can be obtained for pure fcc metals is not a new or particularly noteworthy result. But we note here the small number of adjustable parameters used in the preliminary fit, and that this fit is reasonably good and could not be dramatically improved even by greatly increasing the number of variables. We also note that the physical meaning of two of the adjusted parameters has been generalized from the simple XAFS parameters of Eq. (4.14). Though $\sigma^2$ and $\Delta R$ were altered for each of the twelve paths, their values were governed by the parameters $\theta_D$ and $\alpha$. This gives fewer free parameters in the fit and allows physically meaningful parameters to be measured directly in the fit (and is, in the opinion of the author, one of the best features of FEFFIT).

6.3 High Temperature Analysis of Ag XAFS Data

The temperature dependence of the XAFS for pure Ag at high temperatures will now be used to determine the force constants of the anharmonic one-dimensional effective potential between near-neighbor Ag atoms, as discussed chapter 5. This will demonstrate the method used for measuring these force constants from the XAFS data, and will be done using two slightly different approaches. First, separate fits of individual scans will be done, and the temperature-dependence of the measured XAFS parameters will be interpreted to give of the force constants. Second, a simultaneous fit of all scans will be done, with the functional relationship between force constants and XAFS parameters imposed. The comparison of these two approaches will indicate the level of systematic errors inherent in the analysis method and in the imposed relationships between XAFS cumulants and force constants. Section 6.4 will use the results found here to evaluate the local thermodynamic properties of the near-neighbor bond in Ag, and will compare these results to other measurements.

Two successively measured scans at each of the temperatures 240, 300, 400, 500, 600, 700, and 800K were used. The low-temperature data (at 80 and 180K) were found to be dominated by zero-point motion so that the classical approximations made in chapter 5 were inappropriate for them. Even the 240-K spectra were found to be influenced by zero-point motion (the Einstein temperature of Ag is $\sim 170$K). These scans will be included in the first set of fits. From these, it will be shown that quantum influences are visible for the 240-K data, but that the data for all higher temperatures are well inside the classical regime.
6.3.1 Separate Analysis of High Temperature Ag Data

The temperature-dependence of the XAFS data was found by fitting each of the 14 scans (2 at each of the seven temperatures) separately, varying the same quantities in each of the fits. Each scan was analyzed between $R = [1.70, 3.20] \text{ Å}$, with Fourier transform parameters $k_{\text{min}} = 2.5 \text{ Å}^{-1}$, $k_{\text{max}} = 12.0 \text{ Å}^{-1}$, $dk = 1.5 \text{ Å}^{-1}$, and $w = 2$. An example `feffit.inp` file for these fits is shown in Fig. 6.4. All scans were fit using this input and simply changing the data file name and the temperature. Further explanation of the format and contents of the `feffit.inp` file are given in the program documentation [95]. The important point here is that this analysis is quite simple. Only the first three paths of Table 6.1 are used (though the room temperature lattice constant of 4.09 Å was used in the FEFF calculations), with the leakage from second-neighbor scattering and from the double scattering path of 3 mutual near-neighbors (paths 2 and 3, respectively) being included so as to approximate the leakage from these paths into the first-neighbor shell. No variables are adjusted for these two higher paths, and their mean-square-displacements are given by the Correlated Debye Model with $\theta_D = 225$ K and the temperature of the sample. The analysis of the first shell is also relatively simple, with the standard XAFS parameters varied directly in the fit. The value of $S^2_0$ was set to the value from the analysis of the 80-K data above ($= 0.78$). $\Delta E_0$ was varied in each of the fits, as were the first three cumulants for the near-neighbor distribution. An initial set of fits also included the fourth cumulant, and gave values for $C_4$ that were consistent with zero within the estimated uncertainties (which were on the order of 0.00005 Å$^4$) for all temperatures. The fits shown simply set $C_4$ to zero.

The results for these 14 fits are summarized in Table 6.4, which lists the values for $\Delta E_0$, the three fitted cumulants of the near-neighbor bond, $\epsilon_R$ (the estimated statistical uncertainty in $\chi(R)$ for the data), $\chi^2$, and $R$-factor of the fits as a function of temperature. The results given are combinations of the two fitted spectra for each temperature. Deviations in the results for each parameter between the fits to the two different scans at a particular temperature was always considerably less than the estimated uncertainty in that parameter from either of the individual fits. This indicates that the two scans at each temperature agree better with each other than with the best-fit theory, and that the uncertainty in the fitted parameters is dominated by systematic uncertainties in the theory. Representative fits to the 240-K, 500-K, and 800-K data are shown in Figs. 6.5, 6.6, and 6.7.

By examining the quality of these fits and the temperature variation of the
\begin{verbatim}
%--------------------------------------------------------------- title = Pure Ag at 300K scan #1 data = ../bkg/ag_chi.300 out = 300.dat
%--------------------------------------------------------------- rmin = 1.70    rmax = 3.20 kmin = 2.5    kmax = 12.0    dk = 1.50    kweight = 2
%--------------------------------------------------------------- set s02 = 0.78 set temp = 300 set thetad = 225 set sig_mcmaster = 0.00018 guess e0 = 0.0 guess delr = 0.0 guess sig = 0.0 guess third = 0.0 set fourth = 0.0
%--------------------------------------------------------------- s02 0 s02 e0 0 e0 sigma2 0 debye(temp, thetad) + sig_mcmaster

path 1  ../feff/feff0001.dat delr 1  delr sigma2 1  sig + sig_mcmaster third 1  third fourth 1  fourth

path 2  ../feff/feff0002.dat path 3  ../feff/feff0003.dat
%---------------------------------------------------------------
\end{verbatim}

Figure 6.4: Input file to FEFFIT for fit of Ag at 300K. The fit is done between \( R = [1.70, 3.20] \text{Å} \) on data that is Fourier transformed using \( k_{\text{min}} = 2.50 \text{Å}^{-1}, k_{\text{max}} = 13.50 \text{Å}^{-1}, dk = 1.50 \text{Å}^{-1}, \) and \( k \)-weighting exponent \( w = 2. \Delta E_0 \) and the first three cumulants of the first shell of Ag are varied. The fourth cumulant is set to zero, and \( S_0^2 \) is set to 0.78, as found in the low-temperature analysis. A “McMaster correction” of \( \sigma_{\text{McMaster}}^2 \approx 0.0002 \text{Å}^2 \) is used, as described in section 3.1.
Table 6.4: Results of 14 separate fits to high-temperature Ag data between 240K and 800K. All fits were done between $R = [1.70, 3.20]$ Å, with Fourier transform parameters $k = [2.5, 12.0]$ Å$^{-1}$, $dk = 1.5$ Å$^{-1}$, and $w = 2$. The best-fit values and uncertainties for the first three cumulants of the near-neighbor distribution, $\epsilon_R$ (the measurement uncertainty in $\tilde{\chi}(R)$), and the goodness-of-fit parameters $\chi^2$ and $\mathcal{R}$ are listed. All best-fit values of $\Delta E_0$ for all scans were within the estimated uncertainty ($\sim 1.0$ eV) of each other, and are not listed. The reported values are combinations of two different fits at each of the temperatures.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$C_3$ (Å$^3$)</th>
<th>$\epsilon_R$ (Å$^{-3}$)</th>
<th>$\chi^2$</th>
<th>$\mathcal{R}$</th>
</tr>
</thead>
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<td>240</td>
<td>$-0.006(19)$</td>
<td>$0.0077(03)$</td>
<td>$-0.0000(2)$</td>
<td>$0.0064$</td>
<td>648.</td>
<td>0.008</td>
</tr>
<tr>
<td>300</td>
<td>$-0.017(17)$</td>
<td>$0.0090(03)$</td>
<td>$-0.0002(2)$</td>
<td>$0.0049$</td>
<td>657.</td>
<td>0.006</td>
</tr>
<tr>
<td>400</td>
<td>$-0.016(21)$</td>
<td>$0.0124(04)$</td>
<td>$-0.0000(3)$</td>
<td>$0.0059$</td>
<td>230.</td>
<td>0.006</td>
</tr>
<tr>
<td>500</td>
<td>$-0.013(30)$</td>
<td>$0.0159(06)$</td>
<td>$0.0002(5)$</td>
<td>$0.0066$</td>
<td>156.</td>
<td>0.009</td>
</tr>
<tr>
<td>600</td>
<td>$-0.005(48)$</td>
<td>$0.0194(09)$</td>
<td>$0.0007(8)$</td>
<td>$0.0070$</td>
<td>177.</td>
<td>0.016</td>
</tr>
<tr>
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<td>$0.0231(11)$</td>
<td>$0.0011(12)$</td>
<td>$0.0059$</td>
<td>208.</td>
<td>0.018</td>
</tr>
<tr>
<td>800</td>
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<td>$0.0267(16)$</td>
<td>$0.0017(18)$</td>
<td>$0.0077$</td>
<td>118.</td>
<td>0.029</td>
</tr>
</tbody>
</table>
Figure 6.5: Fit to XAFS $\tilde{\chi}(R)$ for Ag at 240K. The dashed curve shows experimental data; the solid curve shows a fit to the experimental data using first three FEFF paths. Four variables were adjusted in the fit: $\Delta E_0$, $\Delta R_0$, and $\sigma^2$, and $C_3$. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.4.

The goodness-of-fit parameters $\chi^2$ and $R$, the relative importance of systematic and statistical uncertainties can be further explored. The combination of these two different sum of squares of the misfit, with their different scaling factors, gives important clues to the reliability of the various fits and to the sources of the misfit. Table 6.4 shows that $\epsilon_R$ is roughly constant with temperature (or maybe increases slightly), whereas $\chi^2$ decreases dramatically and $R$ increases substantially with temperature. These results indicate that the misfit becomes more influenced by the statistical variations of the data at high temperature, where the signal has decreased to be more comparable to this random noise (at 800K, the rms noise is something like 20% of the rms signal for the first shell). For low-temperatures, on the hand, the signal in the data is so strong compared to the random fluctuations of the data that the misfit is dominated by systematic errors in the model (which is a combination of the theory from FEFF and the choice of variable parameters in the best-fit process). Thus $\chi^2$, which is scaled to the statistical fluctuations $\epsilon_R$, is large for low temperatures and decreases with temperature as the signal (and therefore the mean-square difference of data and model signals) gets smaller. But since the relative misfit of data and model becomes dominated by the random fluctuations in the data itself, $R$, which is scaled to the
Figure 6.6: Fit to XAFS $\tilde{\chi}(R)$ for Ag at 500K. The dashed curve shows experimental data; the solid curve shows a fit to the experimental data using first three FEFF paths. Four variables were adjusted in the fit: $\Delta E_0$, $\Delta R_0$, and $\sigma^2$, and $C_3$. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.4.

ever decreasing average amplitude of the data, grows with increasing temperature.

If the XAFS results for the temperature-dependence of the lowest three cumulants are used with Eq. (5.11), values for the anharmonic force constants can be obtained. Using only the leading term of the first three formulas listed in Eq. (5.11), so that $\sigma^2 = k_B T / a$, $\Delta R = -3b k_B T / a^2$, and $C_3 = -6b (k_B T)^2 / a^3$, we can use linear regression to get the force constant $a$ from the temperature-dependence of $\sigma^2$, and then use this result to evaluate $b$ from either $C_3$ or $\Delta R$. The first of these steps yields $a = 2.52 \pm 0.08 \text{ eV/Å}^2$. This uncertainty is dominated by the systematic error of whether or not to include the lowest temperature data (the uncertainty from the regression itself is on the order of $10^{-5} a$). This is presented in Fig. 6.8, which shows the $\sigma^2$ data from Table 6.4 and two best-fit lines to this data — the dashed line includes the 240-K data point in the fit and the solid line does not. Both of these fits to the temperature-dependence of $\sigma^2$ can be considered good, falling well within the estimated uncertainties for each individual measurement of $\sigma^2$. This is true even at the lower temperatures, where any quantum effects might be expected. Nevertheless, some evidence of zero-point motion can be seen from this plot. The best-fit line which includes the 240-K is consistently too low for the highest three temperatures, too high
Figure 6.7: Fit to XAFS $\tilde{\chi}(R)$ for Ag at 800K. The dashed curve shows experimental data; the solid curve shows a fit to the experimental data using first three FEFF paths. Four variables were adjusted in the fit: $\Delta E_0$, $\Delta R_0$, and $\sigma^2$, and $C_3$. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.4.

for the 300-K, 400-K, and 500-K data, and is too low for the 240-K data. This is just what would be expected from zero-point motion (where the linear behavior of $\sigma^2(T)$ deviates to higher $\sigma^2$ at low-$T$). The best-fit line which ignores the 240-K data (the solid line in Fig. 6.8) is much better over the 300–800K range. This systematic deviation away from the linear dependence of $\sigma^2(T)$ suggests that the 240-K data is still influenced by zero-point motion, and that the classical approximations made in chapter 5 may need some corrections in order to use this data. By ignoring the 240-K data, the best-fit value of $a$ becomes 2.46 eV/Å². This value will be used below, while the uncertainty in this number will be conservatively kept at 0.08 eV/Å².

The value of $a$ found above and linear regression of $\Delta R = -3b k_B T/a^2$ gives $b = -1.2 \pm 0.4$ eV/Å³, with fits illustrated in Fig. 6.9. The uncertainty here has important contributions from the uncertainty in $a$, and in the different fits to $\Delta R(T)$ obtained with and without the 240-K data included in the fit. The root cause of both these contributions is still the systematic uncertainty of whether or not to include the lowest temperature data, and the inclusion of the lower temperature data serves to lower $b$. If $b$ is found instead from the quadratic temperature dependence of $C_3 = -6b (k_B T)^2/a^3$, the 240-K data is less important to the final value, which becomes
Figure 6.8: Temperature dependence of $\sigma^2$ for Ag, found by XAFS analysis. The dashed lines shows a fit to this experimental data using a straight line to all the data. The solid line shows a linear fit to all data except the lowest temperature data, for which quantum effects may still be important.

Figure 6.9: Temperature dependence of $\Delta R$ for Ag, found by XAFS analysis. The dashed lines shows a fit to this experimental data using a straight line to all the data. The solid line shows a linear fit to all data except the lowest temperature data, for which quantum effects may still be important.
Figure 6.10: Temperature dependence of $C_3$ for Ag, found by XAFS analysis. The dashed lines shows a fit to this experimental data using a linear fit in $T^2$ to all the data. The solid line shows a linear fit in $T^2$ to all data except the lowest temperature data, for which quantum effects may still be important.

$b = -0.9 \pm 0.3 \text{eV/Å}^3$, with fits shown in Fig. 6.10. Neither of these fits is as good as that of Fig. 6.8 for $\sigma^2(T)$. The agreement between the two results for $b$ is only marginal, and the uncertainty is fairly large. Still, it should be noted that, again apart from the 240-K data, no obvious systematic deviations from the linear behavior of $\Delta R(T)$ or the quadratic behavior of $C_3(T)$ is seen (with the possible exception that non-zero offsets). In the next subsection, I will see if these rather uncertain values for $b$ can be reduced if we impose the linear temperature dependence of $\sigma^2(T)$ and $\Delta R(T)$ and the quadratic temperature dependence of $C_3(T)$ on the data, and fit the anharmonic force constants to the entire set of temperature-dependent data directly.

### 6.3.2 Simultaneous Analysis of High Temperature Ag Data

The fitting model of the previous section is now expanded to include the temperature dependence of the anharmonic force constants directly. This will be done by simultaneously fitting all high temperature data with cumulants written in terms of these force constants as described in section 5.1. This will provide both a conceptual and utilitarian improvement over the separate fits of the previous section, and will be the model for all further analysis in this work.
Two separately measured scans at temperatures of 300, 400, 500, 600, 700, and 800K were simultaneously fitted to a model consisting of an anharmonic potential for the near neighbor Ag-Ag bond (for a total of 12 $\chi(k)$ spectra). As for the separate fits in the previous section, each scan was analyzed between $R = [1.70, 3.20]$ Å, with Fourier transform parameters $k = [2.50, 12.0]$ Å$^{-1}$, $dk = 1.5$ Å$^{-1}$, and $w = 2$. There were 8 independent points in each of the 12 scans. The data were fitted simultaneously with each data set being equally weighted, so that the total misfit $f$ was a simple sum over the misfit (given in Eq. (4.17)) from each data set.

The three anharmonic force constants ($a$, $b$, and $c$ in Eq. (5.1)), were varied in the fit, and used, along with the known temperature, to give the value for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$ for each temperature, according to Eq. (5.11). Note that $C_4$ was adjusted in these fits. Because an arbitrary near-neighbor distance was used to generate the model XAFS, an additional constant offset to the near-neighbor distance $\Delta R_{\text{off}}$ was allowed to be varied, so that the parameterized form of $\Delta R$ used was

$$\Delta R = \Delta R_{\text{off}} + \frac{-3b k_B T}{a^2} \left[1 + \frac{k_B T}{a^2} \left(\frac{45b^2}{a} - 32c\right)\right]. \quad (6.1)$$

As in the previous section, a fixed value “McMaster correction” was added to the thermal $\sigma^2$, with sized $\sigma^2_{\text{McMaster}} = 0.00018$ Å$^2$. The scans were found to be sufficiently well-aligned in energy that a single variable $\Delta E_0$ was used for all scans. The value $S_0^2$ was also allowed to vary in the fit, giving a total of 6 variables in the fit. Thus, there was enough information in each of the twelve scans to determine each fitting parameter separately, which is essentially what was done in the previous section. But here the force constants can be directly measured using all the temperature dependent data.

The input file to FEFFIT for this simultaneous fit of the temperature-dependent Ag data is considerably more complicated than the simple example feffit.inp shown in Fig. 6.4. Since the fit itself is considerably more complicated, this is probably unavoidable. The complete text of the input files used are given and annotated in Appendix A. These will serve as model input files for all later fits done in this work.

The best-fit values for the three force constants were $a = 2.92 \pm 0.06$ eV Å$^2$, $b = -1.27 \pm 0.18$ eV Å$^3$, and $c = 1.13 \pm 0.51$ eV Å$^4$. $S_0^2$ was found to be $0.79 \pm 0.02$, and the arbitrary offset in near-neighbor distance was $\Delta R_{\text{off}} = -0.005 \pm 0.002$ Å. The single $\Delta E_0$ was found as $\Delta E_0 = -4.01 \pm 0.15$ eV. Significant correlations were found between several pairs of variables: $C(b,c) \approx -0.94$, $C(a,S_0^2) \approx -0.81$, $C(\Delta E_0, \Delta R_{\text{off}}) \approx 0.71$, and $C(a,c) \approx -0.63$. All other correlations were smaller than 0.60. Temperature dependent results for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$ and their uncertainties
Table 6.5: Results of a simultaneous fit to all high-temperature Ag data (between 300 and 800K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters $\chi^2$ and $\mathcal{R}$. Values for $c_R$ are the same as those listed in Table 6.4. Best-fit values for the fitted parameters were $\Delta E_0 = -4.01 \pm 0.15$ eV, $S_0^2 = 0.79 \pm 0.02$, $a = 2.92 \pm 0.06$ eV/Å$^2$, $b = -1.27 \pm 0.18$ eV/Å$^3$, and $c = 1.13 \pm 0.51$ eV/Å$^4$. The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants $a$, $b$, and $c$.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$\Delta R$(Å)</th>
<th>$\sigma^2$(Å$^2$)</th>
<th>$C_3$(Å$^3$)</th>
<th>$C_4$(Å$^4$)</th>
<th>$\chi^2$</th>
<th>$\mathcal{R}$</th>
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<td>0.00004(02)</td>
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</tr>
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<td>0.00015(10)</td>
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</tbody>
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Figure 6.11: 300-K result of a simultaneous fit to XAFS $\tilde{\chi}(R)$ of high temperature Ag, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.5.
Figure 6.12: 500-K result of a simultaneous fit to XAFS $\chi(R)$ of high temperature Ag, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dashed lines. Fit results are given in Table 6.5.

are listed in Table 6.5, along with the goodness-of-fit measures $\chi^2$ and $R$ for the fit at each temperature. The results given are combinations of the two fitted spectra for each temperature, and the results can be directly compared to those in Table 6.4 for the fits to the separate spectra. Representative fits to the 300-K, 500-K, and 800-K data are shown in Figs. 6.11, 6.12, and 6.13.

The measures of the goodness-of-fit for this simultaneous fit are roughly the same as for the fits to the individual scans. The $R$-factors are roughly the same for the two fitting styles ($\sim 0.013$), and are about as good as can be expected for fits of real data to theory. The values of $\chi^2$ are also comparable, even though many fewer variables are used per data set in the simultaneous fit. Despite its great utility for interpreting closely related fits of a single system, values of $\chi^2$ cannot easily be compared for the two different styles of fitting, due mostly to ambiguities in the definition of the amount of information in two scans at different temperatures. $^1$

$^1$ This is a subset of the problem in counting independent points in multiple data sets. For two XAFS scans at the same edge of a single material, it seems unlikely that the amount of information is doubled (consider the case if the two temperatures are 1K apart!). But if a second scan adds no additional information, it will at least improve the measurements of the parameters. Throughout
Figure 6.13: 800-K result of a simultaneous fit to XAFS $\tilde{\chi}(R)$ of high temperature Ag, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.5.

The results found for the physical parameters ($a$, $b$, $c$, $\Delta R_{\text{off}}$, and $S_0^2$) of this simultaneous fit are, on the other hand, significantly different than those found from the temperature dependence of the individually fitted cumulants. This discrepancy points to subtle but important differences in how the two the methods were used to give the force constants. In the earlier fits to the temperature dependence of the cumulants, no constraints were placed between $\Delta R$ and $C_3$, so that two different values of $b$ were found, even though the model of the anharmonic potential clearly indicates that they should be consistent. Furthermore, the second-order terms in temperature in Eq. (5.11) were neglected in the earlier fits, though they give non-negligible corrections at the higher temperatures. The fourth cumulant was also left out of the previous fits, though here they are found to be significantly non-zero at high temperatures.

Perhaps the most important difference, though, is that the fits to the temperature

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this work I will adopt the conservative practice of never fitting more variables to temperature-dependent data than is available in a single scan. But since all the independent points are used to improve the measurements of the bond parameters, uncertainties in the fitted variables will be evaluated using all independent points in all spectra.
dependence of $\sigma^2$ and $C_3$ (shown in Figs. 6.8 and 6.10, respectively) allowed arbitrary offsets. These are not expected for a bond with a single vibrational frequency, either harmonic or anharmonic, and are considered to be non-physical parameters that spoil the determination of the physically meaningful parameters. Simultaneous fits to the temperature-dependent data with adjustable offsets show that such offsets are non-zero but only marginally so. They do not significantly improve the overall quality of the fit. For example, the average $\chi^2$ of the 12 scans is improved by less than a few percent by the addition of an offset in $\sigma^2$, which ends up with a best-fit value of $\sigma^2_{\text{off}} = -0.0010 \pm 0.0008$ Å$^2$. The inclusion of this barely significant offset does effect the values and uncertainties in the best-fit values for $S_0^2$ and $a$, but not dramatically. On the whole, the addition of this offset is found to have a small effect on the quality of the fit, while adding a non-physical parameter to the fit. This non-physical parameter is found to spoil the values for the more physically significant variables. Because of ability to more carefully control and prevent such non-physical parameters in the fit, the results from the simultaneous fits to all the temperature-dependent data are taken as the more reliable results.

6.4 Thermodynamic Parameters for Ag from XAFS Analysis

We can now evaluate thermodynamic parameters for the Ag-Ag bond using the anharmonic force constants measured by XAFS and the development in section 5.2 for the thermodynamics of a bond described by this anharmonic potential. These values can then be compared to those expected from other measurements and calculations. The best-fit values for the force constants from the simultaneous fit to all data scans is felt to be the more reliable set (giving a better fit to all the data scans, and using a more robust model in which unreasonable temperature behavior is forbidden). The values found for the three force constants were $a = 2.92 \pm 0.06$ eV/Å$^2$, $b = -1.27 \pm 0.18$ eV/Å$^3$, and $c = 1.13 \pm 0.51$ eV/Å$^4$. As discussed in chapter 5, these force constants can be used to calculate a variety of thermodynamic properties of the Ag-Ag bond.

First, we calculate the linear thermal expansion coefficient. Following the discussion in section 5.2, this is found from the volume expansion, and is given by Eq. (5.19). Using the above values for $a$ and $b$, and $R_0 = 2.892$ Å (the room temperature near-neighbor distance) in this formula gives $\alpha = 17.0 \pm 2.0 \times 10^{-6}$, which agrees rather well with the known bulk value of $\alpha = 19.2 \pm 1.0 \times 10^{-6}$, found from x-ray diffraction measurements [104]. We note here that the simplified version of the linear expansion
coefficient (which was really the radial expansion coefficient) would dramatically underestimate $\alpha$. Using the simpler formula of Eq. (5.16) gives $\alpha = 13.4 \pm 2.0 \times 10^{-6}$, which does not agree well with the known value. Using this simpler formula for the linear expansion coefficient, Stern, Liviš, and Zhang [39] found an $\alpha$ for pure Pb that was also lower than the known bulk value, though their value was closer than is found here for pure Ag.

Next, we calculate the Einstein temperature in terms of the force constant $a$ using Eq. (5.24). The result is that $\theta_E = 174.3 \pm 1.9$ K. This compares well with the result from bulk heat capacity measurements, which typically give $\theta_E = 175$ K.

Following the discuss of Lottici [35] and Sevillano, et al. [36], the Einstein temperature measured in XAFS measurements can be fairly simply related to the more typically used Debye temperature. Though the conversion factor between the two characteristic temperatures varies a bit on the assumptions made about the phonon dispersion and the temperature limits, the ratio of $\theta_D/\theta_E$ is usually given as between 1.25 and 1.33. Using $\theta_D/\theta_E \approx 1.27$, as suggested by Lottici for this ratio, gives an XAFS-measured Debye temperature of $\theta_D = 221.3 \pm 2.4$ K. This agrees quite well with the usually cited Debye temperature for Ag of 225 K, derived from heat capacity measurements [53].

The Grüneisen parameter, written in Eq. (5.20) in simple terms of the force constants $a$ and $b$, and the equilibrium distance $R_0$, can easily be evaluated as $\gamma = 2.57 \pm 0.17$. This agrees quite well with the usual experimental value of $\gamma \approx 2.5$, as found by measuring the pressure dependence of the bulk compressibility [105, 106]. The agreement here is probably related to the fact that the Einstein model works reasonably well to describe close-packed monoatomic metals, so that the volume dependence of the vibrational modes of the solid can be well-approximated by that of the single major mode. Finally, the bulk modulus for Ag is calculated according to Eq. (5.21) as $K = 0.79 \pm 0.11$ eV/$\text{Å}^3$. This agrees rather well with the value typically found from thermo-elastic measurements for Ag [107, 103], which is $K \approx 0.65$ eV/$\text{Å}^3$. These results will be further discussed at the end of chapter 8.

6.5 High Temperature Analysis of Au XAFS Data

A sample of pure Au was prepared by rolling a piece of 99.9999% Au shot supplied by Johnson Matthey to a thickness of 7 $\mu$m. This gave a total $\mu x$ of 2.4 and $\Delta \mu x$ of 1.5 for the Au $L_{III}$-edge, at 11918 eV. XAFS measurements were made on pure Au in transmission at temperatures of 80, 160, 300, 400, 500, 600, and 700K, at
beamline X-11A of the NSLS using a Si (111) double-crystal, detuned to pass 70% of the incident beam. The same kinds of x-ray detectors and temperature controls used for the pure Ag and described in chapter 3 were used for the XAFS measurements of pure Au.

Figure 6.14 shows the measured absorption spectra of Au at 300K and the background spline put through this data to isolate the structural $\chi(k)$. The background absorption was found for all signals using AUTOBK with $R_{\text{bkg}} = 1.55 \text{Å}$. The temperature dependence of the first shell XAFS of pure Au at 300K, 400K, 500K, 600K, and 700K were simultaneously analyzed using FEFFIT and the same basic procedures described in section 6.3.2. Each scan was analyzed between $R = [1.70, 3.20] \text{Å}$, with Fourier transform parameters $k = [2.75, 13.50] \text{Å}^{-1}$, $dk = 1.5 \text{Å}^{-1}$, and $w = 2$. FEFF calculations for the first three paths (first-neighbor single-scattering, second-neighbor single-scattering, and the double-scattering path involving three mutual near-neighbors) were used in the analysis, and were generated using only the atomic species (Au), absorption edge ($L_{\text{III}}$), crystal structure (fcc), and lattice constant ($4.08 \text{Å}$).

The three anharmonic force constants ($a$, $b$, and $c$ in Eq. (5.1)) were varied in the
Table 6.6: Results of a simultaneous fit to all high-temperature Au data (between 300 and 700K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters $\chi^2$ and $R$. The measurement uncertainty for all data was $\epsilon_R \approx 0.004 \text{Å}^{-3}$. Best-fit values for the fitted parameters were $\Delta E_0 = 1.8 \pm 0.2 \text{eV}$, $S_0^2 = 0.85 \pm 0.02$, $\Delta R_{\text{off}} = -0.011 \pm 0.002 \text{Å}$, $a = 3.33 \pm 0.09 \text{eV/Å}^2$, $b = -1.18 \pm 0.35 \text{eV/Å}^3$, and $c = -1.0 \pm 1.7 \text{eV/Å}^4$. The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants $a$, $b$, and $c$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$C_3$ (Å$^3$)</th>
<th>$C_4$ (Å$^4$)</th>
<th>$\chi^2$</th>
<th>$R$</th>
</tr>
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</table>

Figure 6.15: 300-K result of a simultaneous fit to XAFS $\tilde{\chi}(R)$ of high temperature Au, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.6.
Figure 6.16: 500-K result of a simultaneous fit to XAFS $\tilde{\chi}(R)$ of high temperature Au, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.6.

fit and used to give the XAFS parameters $\sigma^2$, $C_3$, and $C_4$ according to Eq. (5.11). As for the analysis of pure Ag, Eq. (6.1) was used to give $\Delta R$, and $\Delta R_{\text{off}}$ was varied in the fit. A single adjustable $\Delta E_0$ and a single adjustable $S_0^2$ were also allowed to vary in the fit, giving a total of six variables in the fit of five data files, each of which had 10 independent data points.

The best-fit values and estimated uncertainties for the six variables in the fit to the high-temperature Au XAFS data were: $S_0^2 = 0.85 \pm 0.02$, $\Delta E_0 = 1.8 \pm 0.2$ eV, $\Delta R_{\text{off}} = -0.011 \pm 0.002$ Å, $a = 3.33 \pm 0.09$ eV/Å$^2$, $b = -1.18 \pm 0.35$ eV/Å$^3$, and $c = -1.0 \pm 1.7$ eV/Å$^4$. Significant correlations were found between several pairs of variables: $C(b,c) \approx -0.95$, $C(\Delta E_0, \Delta R_{\text{off}}) \approx 0.67$, and $C(a,c) \approx -0.61$. Temperature dependent values for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$, and the goodness-of-fit measures $\chi^2$ and $R$ are listed in Table 6.6. Examples of the fits themselves are shown in Figs. 6.15, 6.16, and 6.17.
Figure 6.17: 700-K result of a simultaneous fit to XAFS $\tilde{\chi}(R)$ of high temperature Au, using 3 anharmonic force constants, $S_0^2$, $\Delta E_0$, and $\Delta R_{\text{off}}$. The dashed curve shows experimental data; the solid curve shows the fit results. $R_{\text{min}}$ and $R_{\text{max}}$ are indicated by dotted lines. Fit results are given in Table 6.6.

6.6 Thermodynamic Parameters for Au from XAFS Analysis

As in section 6.4, thermodynamic parameters for the Au-Au bond can be determined from the XAFS results for the anharmonic force constants. We do that now.

For Au, the XAFS measurements and Eq. (5.19) give $\alpha = 12.7 \pm 2.9 \times 10^{-6}$, while the known bulk value is [104] $\alpha = 14 \pm 1 \times 10^{-6}$. The agreement here is roughly the same as for pure Ag — the value found by XAFS for $\alpha$ is slightly lower than the bulk value, though the disagreement is within the estimated uncertainties. Despite this small but systematic departure from the bulk value, the agreement here is fairly encouraging considering that bulk properties were not used at all in deriving the XAFS measurement of $\alpha$, and that a fairly simple-minded approach to anharmonicity in the near-neighbor bond was used to derive this value.

The Einstein temperature can be found in terms of the force constant $a$ using Eq. (5.24). The result is that $\theta_E = 138.0 \pm 1.8$ K. This compares well with the result from bulk heat capacity measurements, which typically give $\theta_E = 135$ K. It also compares well with earlier XAFS measurements [36, 34] of the Einstein temperature. This corresponds to an XAFS-measured value for the Debye temperature (using $\theta_D/\theta_E \approx$
1.27) of $\theta_D = 175.2 \pm 2.3$ K, which compares quite well with the usually reported value [53] of $\theta_D = 170$ K.

The Grüneisen parameter, written in Eq. (5.20) in simple terms of the force constants $a$ and $b$, and the equilibrium distance $R_0$, can easily be evaluated as $\gamma = 2.95 \pm 0.83$. This agrees quite well with the usual experimental value of $\gamma \approx 3.0$, as found by measuring the pressure dependence of the bulk compressibility [105, 106]. According to Eq. (5.21), the bulk modulus for Au $K = 1.22 \pm 0.44 \text{eV/Å}^3$. This also agrees well (though the error bars are large) with the known value for the bulk modulus $K \approx 1.1 \text{eV/Å}^3$ for Au, found from thermo-elastic measurements [107, 103].
Chapter 7

EMBEDDED-ATOM-MODEL CALCULATIONS FOR PURE AG

The XAFS results for pure Ag in chapter 6 can be checked by comparing to molecular dynamic simulations. The simulations done here use a modified version of the embedded-atom-method (EAM) [6, 7, 8], with potentials created for Ag by the molecular-dynamics group led by H. Jonsson in the chemistry department at the University of Washington [108]. I thank H. Jonsson, S. Shumway, and A. Goldstein for help in these calculations.

The simulations were done on an 8 × 8 × 8 cube of Ag atoms with periodic boundary conditions. The crystal was kept at atmospheric pressure. In order to achieve a system that was in equilibrium at a specific temperature, each atom in the crystal was given velocities based on the Boltzmann distribution for the specified temperature, and the system was allowed to equilibrate. This method of changing temperature (bringing the solid into equilibrium with an external heat bath) was repeated until the temperature and potential energy of the system became stable in time without further interaction with the external heat bath.

After constant temperature and potential energy were reached, data on the pair distribution function of the crystal were found. Simulations were run at nominal temperatures 300K, 400K, 500K, 600K, and 700K. At each stabilized temperature, the system was allowed to evolve without coupling with the external heat bath for 10000 time steps. Positions of all 512 atoms were recorded every 100 time steps. Such evolutions were repeated between 5 and 10 times to give different equilibrium configurations of the near-neighbor radial distributions for each temperature. From these snap-shot configurations, the radial distribution around all atoms in the cluster were found. The moments of the near-neighbor distribution were then found, and the cumulants were calculated using Eq. (2.50).

The results for the near-neighbor distribution from these simulations are illustrated in Figures 7.1, 7.2, and 7.3. The XAFS measurements are shown with + symbols, with uncertainties indicated. The results from the model calculations are shown with ◇ symbols, with each symbol representing the average of 10000 time steps.
Figure 7.1: Comparison of XAFS measurements (+, with uncertainties shown) and molecular-dynamic simulations (◇) using the embedded-atom-model for the first cumulant, $\Delta R$ of pure Ag between 300K and 800K.

Figure 7.2: Comparison of XAFS measurements (+, with uncertainties shown) and molecular-dynamic simulations (◇) using the embedded-atom-model for the second cumulant, $\sigma^2$ of pure Ag between 300K and 800K.
Figure 7.3: Comparison of XAFS measurements (+, with uncertainties shown) and molecular-dynamic simulations (◇) using the embedded-atom-model for the third cumulant, $C_3$ of pure Ag between 300K and 800K.

of the simulation.

Figure 7.1 shows the temperature dependence of the change in average near-neighbor distance for the simulations and those measured by XAFS. The value for $\alpha$ from the simulations is larger than the value from XAFS. The apparent differences in Fig. 7.1 are not reflected strongly in the linear thermal expansion coefficient. While the XAFS-measured values give a coefficient of linear expansion of $\alpha \approx 17 \times 10^{-6}$, the EAM results give $\alpha \approx 20 \times 10^{-6}$ (The bulk value is known to be $\alpha \approx 19 \times 10^{-6}$). The XAFS measurements show a much larger $T^2$ term to the thermal expansion coefficient. But neither the XAFS or the EAM measurements of $\alpha$ is particularly bad, and the disagreement seen in Fig. 7.1 are on either side of the known result. If anything, the EAM results may be better than the XAFS results.

The simulations do worse than the XAFS measurements for the temperature dependence of $\sigma^2$ of the first neighbor, shown in Fig. 7.2. This result is rather surprising, and probably indicates a severe problem in the way the calculations were done. The simulations suggest that Ag has an Einstein temperature of $\theta_E \approx 139$ K, or equivalently, that the Debye temperature is $\theta_D \approx 176$ K. These results are about $\sim 20\%$ lower than the value found by XAFS (which gave $\theta_E \approx 174$ K).

It is possible that the potential is simply not well-scaled to the temperature, and
that the temperatures in the EAM calculations need to be adjusted down by ~ 20%. This would give an Einstein temperature of $\theta_E \approx 174$ K, which are more in keeping with both the XAFS measurements and the bulk properties of the solid. This would, however, lower the linear thermal expansion coefficient to be $\alpha \approx 14 \times 10^{-6}$, which is worse than the value for $\alpha$ with the current temperature scale. So perhaps the temperature scale is well-scaled and the harmonic force constant is too loose in the EAM potential.

Figure 7.3 shows that the third cumulant found by the simulations is comparable in size to that found by XAFS. Though there is not a compelling reason for the sign of $C_3$ being of either sign in the simulations, it does agree with the sign of the XAFS-measured $C_3$. According to the simple potential described in chapter 5, the third cumulant should go as $T^2$, though that is not seen to be the case here.

The result here is that the molecular dynamics simulations do not currently compare well enough with the XAFS data of pure Ag to be useful in interpreting the interatomic forces of Ag. The interatomic potentials in the calculations could probably be improved to more closely reflect the XAFS measurements of $\sigma^2$. Despite, or possibly because of, these confusing initial results, the comparison of molecular dynamic simulations and XAFS seems worth pursuing. If the two methods of analyzing interatomic forces could be reconciled, the simulations would have great utility, especially in the possibility of characterizing the liquid.
Chapter 8

XAFS ANALYSIS OF IMPURITIES IN AG

At this point, the method of using XAFS to measure thermodynamic properties has been presented and shown to give reasonably good agreement with the expected results for pure Ag and Au. In this chapter and the next the newly developed ability of XAFS to measure local thermodynamic quantities will be combined with the well-known ability of XAFS to measure local environments around dilute components in a solid solution. This gives the previously unavailable opportunity to measure local thermodynamic quantities of impurity-host bonds. While the final meaning of the results found here are not completely clear, the ability to measure the potential of mean force (as described in chapter 5) ought to have some application to the theory of binary alloys. It should be especially helpful in constructing the model potentials used by simulations for the study of these systems.

The techniques for determining the anharmonic force constants from the XAFS data and for evaluating the thermodynamic parameters have been sufficiently explained and demonstrated in chapters 5 and 6, so that results can be presented here without too much explanation. This chapter will give the results for impurities in Ag, and the next will give the results for impurities in Au.

Presented below are the analyses and results for XAFS measurements on 5% Ga in Ag, 2.5% Ga in Ag, 5% Sn in Ag, and 5% Au in Ag. All impurities are substitutional in the Ag fcc lattice, and all concentrations are well below the solid solubility limits, so that the alloys are expected to be homogeneous, with the impurities randomly placed in the Ag alloy without any preferential clustering (or anti-clustering) of the impurities. According to x-ray diffraction measurements [104], the distortions to the pure Ag lattice by the addition of these impurities is small, so that the lattice remains fcc and only small modifications to the lattice constant are observed.

The samples were chosen because of their effect on the bulk melting temperature $T_m$ of Ag. Both Ga and Sn impurities lower $T_m$, while Au raises $T_m$ of Ag. In addition, the concentration dependence of the force constants (and the thermodynamic properties of the bond) are checked by examining two different concentrations of Ga impurities. The Sn impurities, though difficult to measure by XAFS, are of special
relevance to the Mössbauer measurements made on the same system [24].

8.1 5% Ga in Ag

A sample of 5% Ga in Ag was prepared for fluorescence XAFS measurements by mixing 99.999% pure Ag shot supplied by United Mineral and Chemical Corp. with 99.999% Ga from ESPI International in a mixture to give a 10 gr sample of 5 at.% Ga\(^1\). As described in section 3.3, the mixture was placed in a quartz tube which was then held under a mechanical vacuum and sealed. The sealed tube was heated over a Bunsen burner to melt the Ga and allow it to wet the Ag shot. The sample was then placed in a furnace and kept at 50 K above the melting temperature of pure Ag (\(\sim 1234 \text{K}\)). The sample temperature was measured and controlled (to within \(\sim 10 \text{K}\) of the target temperature) by thermocouple wire wrapped around the quartz tube. After being held at this temperature for 24 hours, the sample, still in its quartz tube, was quenched directly from the melt into cold water. The quartz tube was then broken, the sample removed, and the ingot mechanically rolled into a foil \(\sim 150 \mu\text{m}\) thick. The foil sample was coated with a thin evaporated layer of aluminum, which was allowed to oxidize by exposing to steam. This aluminum oxide coating, which is impervious to oxygen and will not appreciably mix with the Ag host, prevents the Ga impurities from oxidizing during the high-temperature XAFS measurements.

Fluorescence XAFS measurements were made on the Ga K-edge \((E_K = 10367 \text{eV})\) of this sample at beamline X-11A of the NSLS using a Si (111) double-crystal monochromator. Harmonics were suppressed by detuning the monochromator so as to pass \(\sim 70\%\) of the maximum intensity of the incident beam. The fluorescent intensities were measured using an ion chamber with current pre-amplifier and current-to-voltage amplifier as described in chapter 3 and [66]. To reduce the signal in the fluorescent ion chamber from Compton scattering (and any other non-fluorescent signals), filters and Soller slits were used. Ge is the appropriate filtering element for measuring the Ga K-edge, and the filters used had a total absorption coefficient of about \(\mu x = 1.5\). Further experimental details are given in chapter 3.

XAFS spectra for 5% Ga in Ag were measured at temperatures of 10, 80, 150, 230, 300, 400, 500, 600, 650, 700, 800, and 900 K, with sample temperatures maintained to within 5 K of the nominal values. Measurements were made on two different samples at two different runs (two years apart), and a total of 45 reliable scans of the absorp-

\(^{1}\text{All percentages quoted in this work for the sample concentrations are atomic percent, not weight percent.}\)
Figure 8.1: Measured x-ray absorption spectra for Ga K-edge of 5% Ga in Ag at 300K (solid) and the smooth background (dashed) found by AUTOBK. $R_{\text{bkg}} = 1.50 \, \text{Å}$ was used for all background-removals of Ga impurities in Ag. Leakage from the first shell was modeled by a FEFF calculation for a single Ga atom surrounded by twelve Ag atoms at a distance of $R_0 = 2.89 \, \text{Å}$.

ation edge were made (32 of these were at or above room temperature, and will be used in the high-temperature analysis below). In order to check that sample integrity was maintained throughout the data collection, the samples were re-measured after heating. These measurements verified that the near-neighbor of Ga did not appreciably change during the heating. Most importantly, no oxygen near-neighbors to the gallium were seen, and the overwhelming majority of the near-neighbors were Ag, indicating that there was no separation of phases. But the polycrystalline samples did anneal during the heating. This caused Bragg peaks in the measured absorption spectra, which came from diffraction of the incident x-rays from the larger crystalline grains into the fluorescence ion chamber. Though such Bragg peaks can, in principle, be removed from the spectra\(^2\), this was not done. Other than determining that the Ga was not oxidized and remained mixed in the Ag, these scans were not among the

\(^2\) Bragg peaks, which are highly localized in space, can be eliminated by measuring the spatial dependence of the fluoresced intensity using available technology. For a more thorough explanation of these methods, see Hanske-Petitpierre's thesis [66]. Alternatively, if the Bragg peaks are sufficiently sharp in energy, they can be removed from the data the measurement.
Table 8.1: Results of fits to all high-temperature data on 5% Ga in Ag (between 300 and 900K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters \( \chi^2 \) and \( \mathcal{R} \). The measurement uncertainty for each individual data scan was \( \epsilon_R \approx 0.009 \text{Å}^{-3} \). Best-fit values for the fitted parameters were \( \Delta E_0 = 0.1 \pm 0.2 \text{ eV} \), \( S_0^2 = 0.95 \pm 0.02 \), \( \Delta R_{\text{off}} = -0.039 \pm 0.002 \text{ Å} \), \( x_{\text{Ga}} = 0.042 \pm 0.019 \), \( a = 1.66 \pm 0.04 \text{ eV/Å}^2 \), \( b = -0.61 \pm 0.04 \text{ eV/Å}^3 \), and \( c = 0.51 \pm 0.10 \text{ eV/Å}^4 \). The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants \( a \), \( b \), and \( c \). Values for \( \chi^2 \) and \( \mathcal{R} \) are averages of all fitted scans at the listed temperature.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \Delta R ) (Å)</th>
<th>( \sigma^2 ) (Å²)</th>
<th>( C_3 ) (Å³)</th>
<th>( C_4 ) (Å⁴)</th>
<th>( \chi^2 )</th>
<th>( \mathcal{R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>-0.023(3)</td>
<td>0.0158(04)</td>
<td>0.0005(01)</td>
<td>0.00003(01)</td>
<td>327.</td>
<td>0.010</td>
</tr>
<tr>
<td>400</td>
<td>-0.018(3)</td>
<td>0.0212(06)</td>
<td>0.0008(03)</td>
<td>0.00006(02)</td>
<td>153.</td>
<td>0.007</td>
</tr>
<tr>
<td>500</td>
<td>-0.014(3)</td>
<td>0.0267(08)</td>
<td>0.0012(05)</td>
<td>0.00012(04)</td>
<td>152.</td>
<td>0.009</td>
</tr>
<tr>
<td>600</td>
<td>-0.009(3)</td>
<td>0.0322(11)</td>
<td>0.0017(08)</td>
<td>0.00021(08)</td>
<td>137.</td>
<td>0.012</td>
</tr>
<tr>
<td>700</td>
<td>-0.005(4)</td>
<td>0.0378(14)</td>
<td>0.0022(12)</td>
<td>0.00033(12)</td>
<td>196.</td>
<td>0.024</td>
</tr>
<tr>
<td>800</td>
<td>-0.001(4)</td>
<td>0.0434(17)</td>
<td>0.0027(18)</td>
<td>0.00050(18)</td>
<td>86.</td>
<td>0.018</td>
</tr>
<tr>
<td>900</td>
<td>+0.003(5)</td>
<td>0.0491(21)</td>
<td>0.0033(25)</td>
<td>0.00071(26)</td>
<td>90.</td>
<td>0.026</td>
</tr>
</tbody>
</table>

32 scans used in the analysis described below.

Figure 8.1 shows the measured absorption data for 5% Ga in Ag, and the smooth background absorption as calculated by AUTOBK using \( R_{\text{bkg}} = 1.50 \text{ Å} \). There were 13 degrees of freedom in the background function, and leakage from the first shell into the low-\( R \) region was modeled by a FEFF calculation of a Ga atom surrounded by 12 Ag atoms at a distance of \( R_0 = 2.892 \text{ Å} \) (which is the Ag-Ag near-neighbor distance in pure Ag).

For the high-temperature analysis of the first shell surrounding the Ga atoms in 5% Ga in Ag, 32 scans between 300K and 900K were analyzed. To check for differences between samples and date of data collection, these 32 scans were broken into 4 sets of 16 scans each. Each individual scan was in two of the sets. Two of the four sets were dominated by scans taken on each of the two dates, and the other two sets were random mixtures of scans from different dates. Each set had a fairly complete range of temperatures. The 16 scans in each of the 4 sets were fit simultaneously. Each scan was analyzed between \( R = [1.60, 3.70] \text{ Å} \), with Fourier transform parameters \( k = [2.50, 11.0] \text{ Å}^{-1} \), \( dk = 1.50 \text{ Å}^{-1} \), and \( w = 2 \). There were ten independent points
Figure 8.2: 300-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Ga in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Ga}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.1.

in each data scan. Three of the scans were found to be too noisy to be reliably fit, and were taken out of the final fits (two of these were taken at 500K, and one at 600K on the same sample during the same run; the three scans were taken successively, and appear to have some systematic problem).

The data were fit to the sum of four scattering paths from FEFF, generated by putting a small concentration of Ga atoms in a lattice of pure Ag (fcc, with lattice constant 4.09 Å), and using Ga as the central atom. The first of these paths represented Ga-Ga single scattering at the Ag-Ag near-neighbor distance. The second path was Ga-Ga single scattering, also at the Ag-Ag near-neighbor distance, to represent the small probability ($\sim 5\%$) of a near-neighbor of Ga next to the central Ga atom. The remaining two paths, while not strictly part of the first shell, were used to compensate for leakage from higher shells into the first shell. These paths were a double scattering path of mutual near-neighbors, of which only the central atom was Ga, and a single scattering path of Ga-Ag at the second-neighbor distance. For these two longer scattering paths, the low probability of scattering from a Ga atom was simply ignored. No adjustable parameters which affected the XAFS for these two paths were allowed to vary independently from parameters used for the two paths
Figure 8.3: 500-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Ga in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Ga}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.1.

that made up the first shell.

As for the pure materials in chapter 6, the three anharmonic force constants ($a$, $b$, and $c$ in Eq. (5.1)), were varied in the fit. These were used, along with the known temperature, to give values for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$ for each temperature, according to Eq. (5.11). In order to allow the Ga-Ag near-neighbor distance to vary from that of the Ag-Ag distance in pure Ag (as was used in the model calculation), a constant offset to the near-neighbor distance $\Delta R_{\text{off}}$ was allowed to be varied, so that the parameterized form of $\Delta R$ used was as given by Eq. (6.1). Initially, a separate $\Delta R_{\text{off}}$ was used for the Ga-Ga and Ga-Ga near-neighbors. These were found to be indistinguishable from one another (this was also found to be true at the lower temperatures), and so were simply constrained to be equal in all fits presented here. A fixed value “McMaster correction” of $\sigma_{\text{McMaster}}^2 = 0.00043$ Å$^2$ (as described in chapter 3 and calculated by ATOMS) was added to the thermal $\sigma^2$. For the initial fits, additional and separate constant offsets were added to the each of the $\sigma^2$ for the Ga-Ga and Ga-Ag paths, and were both varied to check if there was significant static disorder around the Ga atoms. These two additional constants were found to be consistent with zero, and were not varied in later fits. The scans were sufficiently well-aligned in energy to
Figure 8.4: 700-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Ga in Ag. \( S_0^2, \Delta E_0, a, b, c, \Delta R_{\text{off}}, \) and \( x_{\text{Ga}} \) were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.1.

allow a single variable \( \Delta E_0 \) to be used for all scans. The value of \( S_0^2 \) was allowed to vary in the fit. Finally \( x_{\text{Ga}} \), the Ga concentration (more precisely, the probability of each near-neighbor being Ga instead of Ag) was also allowed to vary in the fit, giving a total of seven variables in the fit: \( a, b, c, \Delta R_{\text{off}}, \Delta E_0, S_0^2, \) and \( x_{\text{Ga}} \). The fitting model used was similar to that used in chapter 6 and given in Appendix A.

The best-fit values and estimated uncertainties for the seven variables were: \( S_0^2 = 0.95 \pm 0.02, \Delta E_0 = 0.1 \pm 0.2 \text{eV}, \Delta R_{\text{off}} = -0.039 \pm 0.002 \text{Å}, a = 1.66 \pm 0.04 \text{eV}/\text{Å}^2, b = -0.61 \pm 0.04 \text{eV}/\text{Å}^3, c = 0.51 \pm 0.10 \text{eV}/\text{Å}^4, \) and \( x_{\text{Ga}} = 0.042 \pm 0.019 \). Significant correlations were found between several pairs of variables: \( C(b, c) \approx -0.87, C(\Delta E_0, \Delta R_{\text{off}}) \approx 0.81, \) and \( C(a, S_0^2) \approx -0.56 \). Temperature-dependent values for \( \Delta R, \sigma^2, C_3, \) and \( C_4, \) and the goodness-of-fit measures \( \chi^2 \) and \( \mathcal{R} \) are listed in Table 8.1. Examples of the fits are shown in Figs. 8.2, 8.3, 8.4, and 8.5.

The large negative offset in the Ga-Ag near-neighbor distance is worth discussing. It shows that the Ag lattice relaxes and contracts around the Ga impurities. The offset found, \( \Delta R_{\text{off}} = -0.039 \pm 0.02 \text{Å}, \) is much larger than the average contraction of the near-neighbor distance induced by adding Ga impurities to Ag, which is seen by x-ray diffraction to be more like \( -0.003 \text{Å} \) [104] for 5% Ga in Ag. This implies that
Figure 8.5: 900-K result of fit (solid) to experimental XAFS data (dashed) of high
temperature 5% Ga in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Ga}}$ were varied in the
simultaneous fit to the data at all temperatures. The fit range is indicated by dotted
lines, and fit results are given in Table 8.1.

most of the contraction induced by the added impurities happens at the Ga impurities
while the Ag-Ag distance in the alloy remains essentially unchanged from that of pure
Ag. This result is interesting but should but not be particularly surprising. Similar
results for contractions of near-neighbor distances around impurities that are far
in excess of the average contraction of the lattice have been seen by other XAFS
studies. The most notable of these is a recent study by Scheuer and Lengeler [47],
who measured the distortions in near-neighbor distance caused by many different
substitutional impurities in both fcc and bcc elemental metals. There are several
phenomenological descriptions [109, 110] that give qualitative agreement with the
observed contraction or expansion.

The Ga concentration, $x_{\text{Ga}}$, is fit to remarkably high precision, and is found to
be very close to the concentration aimed for in the sample preparation. This result
is consistent with there being no clustering or anti-clustering of Ga impurities. The
precision here is a result of the large difference in the backscattering amplitude and
phase-shifts ($f$ and $\delta$) between Ga and Ag, which allows the XAFS signals from the
two atomic species to be easily distinguished in the fit.

As in chapter 6, thermodynamic quantities can be determined from the anhar-
monic force constants for the Ga-Ag bond. The linear thermal expansion coefficient (well, here this would be the temperature-dependent change in the Ga-Ag bond length, which would affect the thermal expansion coefficient of the alloy only to the extent that it is different from the temperature-dependent change in the Ag-Ag bond length), is found by Eq. (5.19) to be $\alpha = 26.4 \pm 1.7 \times 10^{-6}$. This value is considerably larger than the value found for pure Ag. No known bulk value could be found for this bond or even the Ga-Ag alloy as whole, though Pearson [104] does show that the thermal expansion coefficient of most Ag-based alloys is very similar to that of pure Ag, especially at low solute concentrations.

The Einstein temperature of the Ga-Ag bond is found using Eq. (5.24) as $\theta_E = 148.4 \pm 1.8$ K. This is significantly lower than the Einstein temperature for the Ag-Ag bond (which was $\theta_E = 174.3 \pm 1.9$ K), indicating that the Ga-Ag bond is less rigid than the Ag-Ag bond. This Einstein temperature would correspond to a Debye temperature for the Ga-Ag bond of $\theta_D \approx 188.5$ K.

The Grüneisen parameter for the Ga-Ag bond is found from Eq. (5.20) to be $\gamma = 2.91 \pm 0.18$. This is a bit larger than the value of $\gamma \approx 2.57$ found for pure Ag. The bulk modulus for Ga-Ag bond is found from Eq. (5.21) to be $K = 0.59 \pm 0.05$ eV/Å$^3$, which is smaller than that of pure Ag (which was found to be $K \approx 0.79$ eV/Å$^3$), but not dramatically so. Both of these results indicate a looser bond between Ga and Ag than between Ag and Ag.

### 8.2 2.5% Ga in Ag

A sample of 2.5% Ga in Ag was prepared for fluorescence measurements using the same processes to make the 5% Ga in Ag sample, with only the relative weights of Ga and Ag altered. Fluorescence XAFS measurements were made on the Ga $K$-edge using an experimental set-up that was essentially identical to that of the 5% Ga in Ag samples. Ge filters were used to reject non-fluoresced x-rays.

Measurements were made at temperatures 80, 150, 230, 300, 400, 500, 600, and 700K. As with the 5% Ga in Ag, scans at room temperature were taken after heating the sample, and while these measurements showed no evidence of oxidation or separation of phases, they contained Bragg peaks and so were not used included in the high-temperature analysis. 19 scans between 300K and 700K were used for the high-temperature analysis.

Figure 8.6 shows the measured absorption for 2.5% Ga in Ag at 300K, and the smooth background through the data as found by AUTOBK using $R_{bkg} = 1.50$ Å.
Figure 8.6: Measured x-ray absorption spectra for Ga $K$-edge of 2.5% Ga in Ag at 300K (solid) and the smooth background (dashed) found by AUTOBK. $R_{bkg} = 1.50$ Å was used for all background-removals of Ga impurities in Ag. Leakage from the first shell was modeled by a FEFF calculation for a single Ga atom surrounded by twelve Ag atoms at a distance of $R_o = 2.89$ Å.

Leakage from the first shell into the low-$R$ region was modeled by a FEFF calculation of a Ga atom surrounded by 12 Ag atoms at the Ag-Ag distance of $R_o = 2.892$ Å. Note that the scale of the $\mu x$ axis is arbitrary in fluorescence XAFS measurements, and that it is not an absolute measurement of the absorption coefficient. The fact that the scale of $\mu x$ for the 2.5% sample is larger than that for the 5% sample does not indicate that the fluorescent probability is greater, but rather that the amplifier gains were different for the two measurements and not factored out of either one.

The data were fit using the same scattering paths and fitting model used for the 5%Ga in Ag of the previous section, with the same adjustable parameters. Each scan was analyzed between $R = [1.60, 3.70]$ Å, with Fourier transform parameters $k = [2.50, 11.0]$ Å$^{-1}$, $dk = 1.50$ Å$^{-1}$, and $w = 2$, giving ten independent points in each data scan. 19 scans between 300K and 700K were fit simultaneously. Three separate variable $\Delta E_0$ were used for data taken at different synchrotron trips, and for data which was poorly aligned.

The best-fit values and estimated uncertainties for the six important variables for 2.5%Ga in Ag were: $S_0^2 = 0.96 \pm 0.03$, $\Delta R_{eff} = -0.030 \pm 0.004$ Å, $a = 1.60 \pm$
Table 8.2: Results of fits to all high-temperature data on 2.5% Ga in Ag (between 300 and 700K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters \( \chi^2 \) and \( \mathcal{R} \). The measurement uncertainty for each individual data scan was \( \varepsilon_R \approx 0.15 \text{Å}^{-3} \). Best-fit values for the fitted parameters were \( S_0^2 = 0.96 \pm 0.03 \), \( \Delta R_{\text{off}} = -0.030 \pm 0.004 \text{Å} \), \( x_{\text{Ga}} = 0.006 \pm 0.03 \), \( a = 1.60 \pm 0.06 \text{eV/Å}^2 \), \( b = -0.61 \pm 0.06 \text{eV/Å}^3 \), and \( c = 0.70 \pm 0.12 \text{eV/Å}^4 \). Three different \( \Delta E_0 \) were allowed to vary, because of poorly aligned data. The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants \( a \), \( b \), and \( c \). Values for \( \chi^2 \) and \( \mathcal{R} \) are averages of all fitted scans at the listed temperature.

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \Delta R ) (Å)</th>
<th>( \sigma^2 ) (Å²)</th>
<th>( C_3 ) (Å³)</th>
<th>( C_4 ) (Å⁴)</th>
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<th>( \mathcal{R} )</th>
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<td>0.0376(20)</td>
<td>0.0012(23)</td>
<td>0.00030(20)</td>
<td>135.</td>
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0.05 \text{eV/Å}^2 \), \( b = -0.64 \pm 0.06 \text{eV/Å}^3 \), \( c = 0.70 \pm 0.12 \text{eV/Å}^4 \), and \( x_{\text{Ga}} = 0.006 \pm 0.03 \). The three variable \( \Delta E_0 \) were all within 3.0eV of each other, and each had an uncertainty of \( \sim 1 \text{eV} \). Significant correlations were found between several pairs of variables: \( C(b,c) \approx -0.88 \), \( C(a,S_0^2) \approx -0.54 \), and \( C(\Delta E_0, \Delta R_{\text{off}}) \approx 0.72 \), for the \( \Delta E_0 \) that was used in most (14 of the 22) scans. Temperature dependent values for \( \Delta R \), \( \sigma^2 \), \( C_3 \), and \( C_4 \), and the goodness-of-fit measures \( \chi^2 \) and \( \mathcal{R} \) are listed in Table 8.2. Examples of the fits are shown in Figs. 8.7, 8.8, and 8.9. The data is considerably more noisy than the 5%Ga in Ag data, as can clearly be seen from the large random noise in the 700-K data.

As for the 5%Ga in Ag, a large negative offset in the Ga-Ag near-neighbor distance is found, with the value here being \( \Delta R_{\text{off}} = -0.030 \pm 0.04 \text{Å} \), which is slightly smaller than the value found for 5% Ga in Ag, but still significantly larger than the average near-neighbor contraction of the alloy. X-ray diffraction results for the lattice contraction of Ag with small concentrations of impurities typically show a linear dependence on the impurity concentration, at least in the dilute limit [104]. The result here is reasonably consistent with that finding, and the implication found from the 5% Ga in Ag that most of the lattice contraction happens at the Ga impurities while
Figure 8.7: 300-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 2.5% Ga in Ag. $S_0^2$, 3 $\Delta E_0$s, a, b, c, $\Delta R_{\text{off}}$, and $x_{\text{Ga}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.2.

The Ag-Ag distance in 5%Ga in Ag remains essentially unchanged. It appears that the contraction in the Ga-Ag distance depends only weakly on the Ga concentration.

The Ga concentration itself $x_{\text{Ga}}$ was found to be lower than expected, but within the estimated uncertainty of the concentration aimed for in the sample preparation. Of course, the value found is also consistent with zero Ga concentration, indicating that practically none of the scattering atoms are Ga.

The thermodynamic quantities for the Ga-Ag bond in the alloy of 2.5% Ga in Ag are found to be quite similar to those for the Ga-Ag bond in the 5% alloy. Thus, the linear thermal expansion coefficient for this bond is $\alpha = 29.3 \pm 2.7 \times 10^{-6}$, the Einstein temperature is $\theta_E = 145.8 \pm 2.4$ K, the Grüneisen parameter is $\gamma = 2.71 \pm 0.16$, and the bulk modulus is $K = 0.49 \pm 0.06$ eV/Å$^3$. All of these numbers agree with the values found from the 5% alloy within the estimated uncertainties. The conclusion we’re left to draw is that the dynamic properties of Ga-Ag bonds do not depend on Ga concentration, at least to the sensitivity of the measurements here.
Figure 8.8: 500-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 2.5% Ga in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{eff}}$, and $x_{\text{Ga}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.2.

Figure 8.9: 700-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 2.5% Ga in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{eff}}$, and $x_{\text{Ga}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.2.
8.3 5% Sn in Ag

A sample of 5% Sn in Ag was prepared by the same processes used to make the 5% Ga in Ag sample. The weights of Sn and Ag were chosen to give a 10 gr sample at 5 at.%. Sn shot was supplied by Johnson Matthey, with a purity of 99.999%. The Ag used was from 99.999% Ag shot supplied by United Mineral and Chemical Corp. Samples were made for transmission measurements by rolling the alloy to a thickness of 50 μm, which gives a total absorption length of \( \mu x \approx 2.05 \) and an edge step of \( \Delta \mu x \approx 0.10 \). As for the Ga-Ag alloys, the sample was coated with aluminum oxide to prevent oxidation of Sn during the high-temperature XAFS measurements.

The fact that transmission measurements were made requires some special explanation. According to the discussion in section 3.1.4 that led up to Eq. (3.6) (which gave a way to decide whether fluorescence or transmission measurements would be preferable for a given system), fluorescence is marginally better than transmission measurements, at least in the absence of non-statistical noise. But the photon flux at currently available synchrotrons is rather low at the Sn K-edge \( (E_K = 29200\text{ eV}) \), so statistical noise may not dominate the measurement uncertainties. In addition, because the Sn K-edge is not far past the Ag K-edge \( (E_K = 25514\text{ eV}) \), the absorption cross-section of Ag is rather high at these energies. But the most serious problem for doing fluorescence measurements on the system is finding a suitable filter to block the non-fluoresced x-rays. Either In \( (E_K = 27940\text{ eV}) \) or Cd \( (E_K = 26711\text{ eV}) \) can be filters for Sn, as both will absorb the elastic (and nearly elastic) scattered radiation at and above the Sn K-edge while will pass essentially all of the Sn fluorescence \( (E_\alpha = 25270\text{ eV}) \). Unfortunately, the filters will also pass the fluorescence of the excited Ag K-edge \( (E_\alpha = 22162\text{ eV}) \). There is no filter which will pass the Sn fluorescence but absorb the Ag fluorescence. Since each Ag atom is roughly as absorbing as a Sn atom at the Sn K-edge (the ratio of the Sn and Ag cross-sections is \( \sim 1.2 \) at 30000 eV), and since there are 19 Ag atoms for every Sn atom, the signal passed by any filter into the fluorescence ion chamber will be dominated by the uninteresting Ag fluorescence. The result is that fluorescence measurements (which were, in fact, made) are too noisy to be analyzed. The signal-to-noise ratio, though low, is much better for transmission measurements.

Transmission XAFS measurements were made on the Sn K-edge \( (E_K = 29200\text{ eV}) \) of this sample at beamline X-11A of the NSLS using a Si (311) double-crystal monochromator. The few harmonics there are in the beam at such high energies were suppressed by detuning the monochromator so as to pass \( \sim 85\% \) of the maxi-
minimum intensity of the incident beam. The experimental and measurement set-up was similar to that of pure Ag, which was also measured in transmission.

Scans were taken at temperatures of 20, 150, 300, 500, 700, and 850K. Figure 8.10 shows the measured absorption for 5% Sn in Ag at 300K, and the smooth background through the data as found by AUTOBK using $R_{\text{bkg}} = 1.50 \text{Å}$. Leakage from the first shell into the low-$R$ region was modeled by a FEFF calculation for a single Sn atom surrounded by twelve Ag atoms a distance of $R_0 = 2.892 \text{Å}$.

The data were fit using geometrically equivalent scattering paths to those in the Ga-Ag systems (Sn-Ag near-neighbors, Sn-Sn near-neighbors, Sn-Ag second neighbors and a double scattering path involving mutual near-neighbors, of which only the central atom was Sn). Each scan was analyzed between $R = [1.70, 3.30] \text{Å}$, with Fourier transform parameters $k = [2.50, 10.50] \text{Å}^{-1}$, $dk = 1.50 \text{Å}^{-1}$, and $w = 2$. There were eight independent points in each data scan. Nine scans between 300K and 850K were fit simultaneously. The scans were sufficiently aligned in energy that a single variable $\Delta E_0$ was used for all data. The same fitting model used for the systems above was used here, with the same adjustable parameters: $S_0^2$, $\Delta E_0$, $\Delta R_{\text{off}}$, 

$\mu x$ vs $E$ (eV)

Figure 8.10: Measured x-ray absorption spectra for Sn $K$-edge of 5% Sn in Ag at 300K (solid) and the smooth background (dashed) found by AUTOBK. $R_{\text{bkg}} = 1.50 \text{Å}$ was used for all background-removals of Sn impurities in Ag. Leakage from the first shell was modeled by a FEFF calculation for a single Sn atom surrounded by twelve Ag atoms at a distance of $R_0 = 2.89 \text{Å}$. 

Table 8.3: Results of fits to all high-temperature data on 5\% Sn in Ag (between 300 and 850K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters $\chi^2$ and $\mathcal{R}$. The measurement uncertainty for each individual data scan was $\epsilon_R \approx 0.02\text{Å}^{-3}$. Best-fit values for the fitted parameters were $\Delta E_0 = -0.1 \pm 0.5 \text{eV}$, $S_0^2 = 0.90 \pm 0.05$, $\Delta R_{off} = +0.06 \pm 0.01 \text{Å}$, $a = 2.52 \pm 0.18 \text{eV/Å}^2$, $b = -0.91 \pm 0.46 \text{eV/Å}^3$, and $c = 0.0 \pm 1.6 \text{eV/Å}^4$. The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants $a$, $b$, and $c$. Values for $\chi^2$ and $\mathcal{R}$ are averages of all fitted scans at the listed temperature.

<table>
<thead>
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Figure 8.11: 300-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5\% Sn in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, and $\Delta R_{off}$ were varied in the simultaneous fit to the data at all temperatures ($x_{\text{Sn}}$ was set to 0.05). The fit range is indicated by dotted lines, and fit results are given in Table 8.3.
Figure 8.12: 500-K result of fit (solid) to experimental XAFS data (dashed) of high
temperature 5% Sn in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, and $\Delta R_{\text{off}}$ were varied in the simultaneous
fit to the data at all temperatures ($x_{\text{Sn}}$ was set to 0.05). The fit range is indicated by
dotted lines, and fit results are given in Table 8.3.

and the three anharmonic force constants $a$, $b$, and $c$. The Sn concentration, $x_{\text{Sn}}$, was
varied in the initial fits.

The best-fit values and estimated uncertainties for the variables in the fit to the
high-temperature 5% Sn in Ag XAFS data were: $S_0^2 = 0.90 \pm 0.05$, $\Delta E_0 = -0.1 \pm
0.5$ eV, $\Delta R_{\text{off}} = 0.06 \pm 0.01$ Å, $a = 2.52 \pm 0.18$ eV/Å², $b = -0.91 \pm 0.46$ eV/Å³, and $c =
0.0 \pm 1.6$ eV/Å⁴. In initial fits, $x_{\text{Sn}}$ was varied and was found to be $x_{\text{Sn}} = 0.12 \pm 0.23$.
The large uncertainty in $x_{\text{Sn}}$ is discussed below. Though it was most highly correlated
with $\Delta E_0$, and had little effect on the best-fit values of the other parameters, the large
uncertainty found from fitting the XAFS data is actually larger than the uncertainty
in the Sn concentration from the direct measurement of the edge step (as detailed
below). Therefore, the values and uncertainties for the other fitted parameters were
found with $x_{\text{Sn}}$ fixed at 0.05. Temperature dependent values for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$,
and the goodness-of-fit measures $\chi^2$ and $R$ are listed in Table 8.3. Examples of the
fits are shown in Figs. 8.11, 8.12, 8.13, and 8.14.

The Sn concentration $x_{\text{Sn}}$ in Sn-Ag is not measured very reliably with XAFS.
The sensitivity in the Ga concentration above was based on the large differences
in backscattering amplitude and phase-shift ($f$ and $\delta$) between Ga and Ag atoms.
Figure 8.13: 700-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Sn in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, and $\Delta R_{\text{off}}$ were varied in the simultaneous fit to the data at all temperatures ($x_{\text{Sn}}$ was set to 0.05). The fit range is indicated by dotted lines, and fit results are given in Table 8.3.

Figure 8.14: 850-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Sn in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, and $\Delta R_{\text{off}}$ were varied in the simultaneous fit to the data at all temperatures ($x_{\text{Sn}}$ was set to 0.05). The fit range is indicated by dotted lines, and fit results are given in Table 8.3.
But the differences in these scattering factors (which depend most strongly on the density of core electrons in the atoms) are much smaller between Sn and Ag, and the sensitivity vanishes. Fortunately, the relative concentration of Sn in the Sn-Ag sample can be determined reliably from the ratio of the edge step to the total absorption coefficient in a transmission measurement. A 50 µm thick sample of 5% Sn in Ag gives a total absorption length of $\mu x \approx 2.05$ and an edge step of $\Delta \mu x \approx 0.10$. The sample thickness is easily measured, and the edge step can be seen directly from Fig. 8.10 to be $\sim 0.1$ (more precise determination of the edge-step from AUTOBK gives $\Delta \mu x(E_0) = 0.12 \pm 0.01$), so that the Sn concentration can reliably be determined to be $x_{\text{Sn}} = 0.05 \pm 0.02$. It is, however, still quite difficult to determine from the XAFS measurements whether (or to what extent) the Sn and Ag are randomly mixed or whether the solid solution has separated into two phases. The solubility limit of Sn in Ag is usually quoted as 8% at room temperature (it increases slightly with temperature) [1]. The absorption measurements show a concentration smaller than the solubility limit, and the near-neighbor distance for pure Sn is quite different from that of pure Ag, both of which indicate that mixture is homogeneous. Furthermore, the XAFS measurements do favor Ag backscattering over Sn backscattering (though with admittedly large uncertainties). From these different pieces of evidence, it is presumed that the solution has not separated into a Sn-rich and a Ag-rich phase, and that the system is a homogeneous mixture of Sn impurities randomly placed in a Ag lattice.

As with the Ga impurities, the $\Delta R_{\text{off}}$ is significantly different from zero, but here the lattice expands around the Sn impurity, so that $\Delta R_{\text{off}}$ is positive. The average expansion of the Sn-Ag lattice seen by x-ray diffraction [104] gives a change in the average near-neighbor distance of $\sim +0.010$ Å for Sn concentrations of a few percent. The XAFS results are seen to be in keeping with the general trend of the deformation in lattice constant being amplified at the impurity.

The thermodynamic quantities of the Sn-Ag bond in the alloy of 5% Sn in Ag are found using the methods discussed in chapter 5. The linear thermal expansion coefficient for this bond is $\alpha = 16.6 \pm 6.6 \times 10^{-6}$, which is similar to what was found for pure Ag, though admittedly more uncertain. The Einstein temperature for the Sn-Ag bond is $\theta_E = 158.4 \pm 5.8$ K. The Grüneisen parameter is $\gamma = 2.84 \pm 1.15$, and the bulk modulus is found to be $K = 0.84 \pm 0.48 \text{eV/Å}^3$, both of which are reasonably close to the values of pure Ag.

The basic result here is that the Sn-Ag bond is similar to the Ag-Ag bond. The fits to the Sn-Ag data are not very good, so that the fitted parameters are quite
uncertain. This is mostly due to noisy data, but is also at least partly due to misfit in the low-\(R\) region of the first shell, which may indicate a small amount of oxygen near the tin impurities. This does not show up in the low temperature data, or even the room temperature data, and may indicate that the tin impurities oxidized during the high temperature measurements.

8.4 5% Au in Ag

A sample of 5% Au in Ag was prepared for fluorescence measurements by the same basic processes used to make the 5% Ga in Ag sample, with only the weights of Au and Ag chosen to give a sample of 10 gr at 5 at.%. The Au used was from 99.999% Au shot supplied by Johnson Matthey, and the Ag used was from 99.999% Ag shot supplied by United Mineral and Chemical Corp. After weighing, the mixture was sealed in a quartz tube, held in a furnace kept \(\sim 50\) K above the melting temperature of Au (which, at 1340 K, is 100 K higher than the melting temperature of Ag) for 24 hours, and then quenched into water. The sample was rolled into a foil \(\sim 150\) µm thick, and coated with aluminum oxide.

Fluorescence XAFS measurements were taken on the Au \(L_{III}\)-edge (at \(E_{L_{III}} = 11918\) eV) of this sample at beamline X-11A of the NSLS using a Si (111) double-crystal monochromator. Harmonics were suppressed by detuning the monochromator so as to pass \(\sim 75\)% of the maximum intensity of the incident beam. The experimental and measurement set-up was similar to that of the 5% Ga in Ag samples, including Soller slits and filters to block the non-fluoresced x-rays. Ge is the appropriate filtering atom for measuring fluorescence from the Au \(L_{III}\)-edge, and the filters used had a total absorption coefficient of about \(\mu x = 1.0\) at that edge.

Data were taken at 80, 180, 300, 373, 400, 450, 500, 533, 600, 700, 800, and 900K on three different synchrotron trips. Scans were taken after heating the sample, and while these measurements showed no evidence of oxidation or separation of phases (neither Au nor Ag oxidizes, and there is no phase separation for these metals, but these scans were taken anyway and show no unusual behavior), they did contain Bragg peaks and so were not included in the high-temperature analysis. 38 scans between 300K and 900K were used for the high-temperature analysis.

Figure 8.15 shows the measured absorption for 5% Au in Ag at 300K, and the smooth background through the data as found by AUTOBK using \(R_{bkg} = 1.50\) Å. Leakage from the first shell into the low-\(R\) region was modeled by a FEFF calculation of a Au atom surrounded by 12 Ag atoms at the nominal distance of \(R_0 = 2.892\) Å.
Figure 8.15: Measured x-ray absorption spectra for Au $L_{III}$-edge of 5\% Au in Ag at 300K (solid) and the smooth background (dashed) found by AUTOBK. $R_{bkg} = 1.50 \AA$ was used for all background-removals of Au impurities in Ag. Leakage from the first shell was modeled by a FEFF calculation for a single Au atom surrounded by twelve Ag atoms at a distance of $R_0 = 2.89 \AA$.

The data were fit using geometrically equivalent scattering paths to those in the earlier analyses (Au-Ag near-neighbors, Au-Au near-neighbors, Au-Ag second neighbors and a double scattering path involving mutual near-neighbors, of which only the central atom was Au). Each scan was analyzed between $R = [1.70, 3.30] \AA$, with Fourier transform parameters $k = [2.50, 11.0] \AA^{-1}$, $dk = 1.50 \AA^{-1}$, and $w = 2$. There were ten independent points in each data scan. The 38 scans between 300K and 700K were broken into four groups, with each scan in two of the groups. The scans in each of the four groups were fitted simultaneously. The scans were well-aligned in energy so that a single variable $\Delta E_0$ was used for all data. The same basic fitting model for the systems above was used here with adjustable parameters: $S_0^2$, $\Delta E_0$, $x_{Au}$, $\Delta R_{off}$, and the three anharmonic force constants $a$, $b$, and $c$.

The best-fit values and estimated uncertainties for the variables in the fit to the high-temperature 5\% Au in Ag XAFS data were: $S_0^2 = 0.82 \pm 0.02$, $\Delta E_0 = -0.6 \pm 0.2$ eV, $\Delta R_{off} = -0.020 \pm 0.002 \AA$, $a = 3.26 \pm 0.07$ eV/Å$^2$, $b = -1.57 \pm 0.07$ eV/Å$^3$, $c = 1.37 \pm 0.42$ eV/Å$^4$, and $x_{Au} = 0.12 \pm 0.03$. Temperature-dependent values for $\Delta R$, $\sigma^2$, $C_3$, and $C_4$, and the goodness-of-fit measures $\chi^2$ and $R$ are listed in Table
Table 8.4: Results of fits to all high-temperature data on 5% Au in Ag (between 300 and 900 K). Listed are the best-fit values and uncertainties for the first four cumulants of the near-neighbor distribution, and the goodness-of-fit parameters $\chi^2$ and $\mathcal{R}$. The measurement uncertainty for each individual data scan was $\epsilon_R \approx 0.008 \text{Å}^{-3}$. Best-fit values for the fitted parameters were $\Delta E_0 = -0.6 \pm 0.2 \text{eV}$, $S_0^2 = 0.82 \pm 0.02$, $\Delta R_{\text{off}} = -0.020 \pm 0.002 \text{Å}$, $x_{\text{Au}} = 0.12 \pm 0.03$, $a = 3.26 \pm 0.07 \text{eV/Å}^2$, $b = -1.57 \pm 0.07 \text{eV/Å}^3$, and $c = 1.37 \pm 0.42 \text{eV/Å}^4$. The uncertainties listed below for the cumulants are derived from the best-fit values and uncertainties in the force constants $a$, $b$, and $c$. Values for $\chi^2$ and $\mathcal{R}$ are averages of all fitted scans at the listed temperature.

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<td>0.0167(05)</td>
<td>0.0071(22)</td>
<td>0.00006(2)</td>
<td>213.</td>
<td>0.025</td>
</tr>
<tr>
<td>700</td>
<td>+0.005(3)</td>
<td>0.0197(07)</td>
<td>0.0096(34)</td>
<td>0.00010(3)</td>
<td>178.</td>
<td>0.045</td>
</tr>
<tr>
<td>800</td>
<td>+0.009(4)</td>
<td>0.0226(08)</td>
<td>0.0125(50)</td>
<td>0.00014(4)</td>
<td>535.</td>
<td>0.041</td>
</tr>
<tr>
<td>900</td>
<td>+0.012(4)</td>
<td>0.0257(10)</td>
<td>0.0157(69)</td>
<td>0.00020(5)</td>
<td>490.</td>
<td>0.038</td>
</tr>
</tbody>
</table>

8.4. Examples of the fits are shown in Figs. 8.16, 8.17, 8.18, and 8.19.

It is remarkable that the value found here for $S_0^2$ is essentially the same value found for pure Au (within the estimated uncertainties). While $S_0^2$ is in principle a function of only the central atom and should not vary with chemical or physical environment, the result that $S_0^2$ is found to be the same in both transmission and fluorescence measurements is impressive. The amplitude corrections in XAFS data, especially when comparing fluorescence and transmission measurements, are large.

As with the Ga impurities, $\Delta R_{\text{off}}$ is significantly less than zero. And, again, the contraction around the Au impurity is considerably larger than the average contraction of the Au-Ag lattice seen by x-ray diffraction [104], which gives a change in the average near-neighbor distance of $\sim -0.001$ Å for 5% Au in Ag.

The measured Au concentration is considerably higher than intended in sample preparation. XAFS measurements are unable to determine if the total Au concentration in the sample was too high or if there was preferential clustering of Au atoms in the solid solution. Since there is no other evidence that Au atoms cluster in Ag-Au solutions and no phase separation for these metals, it seems most likely that the
Figure 8.16: 300-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Au in Ag. $S^2_0$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Au}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.4.

Figure 8.17: 500-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Au in Ag. $S^2_0$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Au}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.4.
Figure 8.18: 700-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Au in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Au}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.4.

Figure 8.19: 900-K result of fit (solid) to experimental XAFS data (dashed) of high temperature 5% Au in Ag. $S_0^2$, $\Delta E_0$, $a$, $b$, $c$, $\Delta R_{\text{off}}$, and $x_{\text{Au}}$ were varied in the simultaneous fit to the data at all temperatures. The fit range is indicated by dotted lines, and fit results are given in Table 8.4.
sample was made incorrectly.

The thermodynamic quantities of the Au-Ag bond in the alloy of 5% Au in Ag are found as discussed in chapter 5. The linear thermal expansion coefficient is found to be \( \alpha = 16.7 \pm 0.9 \times 10^{-6} \), which is similar to the values found for pure Ag and Au. The Einstein temperature is \( \theta_E = 162.1 \pm 1.9 \)K, the Grüneisen parameter is \( \gamma = 2.47 \pm 0.05 \), and the bulk modulus is \( K = 0.79 \pm 0.05 \text{eV/Å}^3 \). These three different measures of bond strength are closer to those of pure Ag (\( \theta_E \approx 174 \)K, \( \gamma \approx 2.57 \), and \( K \approx 0.79 \text{eV/Å}^3 \)) than those of pure Au (\( \theta_E \approx 138 \)K, \( \gamma \approx 3.0 \), and \( K \approx 1.2 \text{eV/Å}^3 \)).

8.5 Summary of Results for Impurities in Ag

The vibrational and thermodynamic properties of the impurities in Ag found in the previous sections will now be summarized. These results will be compared to one another and to those for pure Ag. Table 8.5 gives a summary of the offsets in near-neighbor distance \( \Delta R_{\text{off}} \) and the three anharmonic force constants for each of the bonds measured.

Figure 8.20 shows the resulting curves for the potential \( \psi(R) \) derived from the best-fit values of \( \Delta R_{\text{off}} \) and the three anharmonic force constants. Though the uncertainties are not explicitly shown, they can be estimated by looking at the difference between the potentials for the two different concentrations of Ga, which are seen to be quite similar, and have potential parameters within each others estimated uncertainties. The Ga-Ag bond is seen to be much looser than the pure Ag bond, while the Au-Ag bond is seen to be slightly tighter than the pure Ag bond. The Sn-Ag bond is significantly displaced from the pure Ag-Ag distance, and is slightly more shallow than the Ag-Ag potential. These observations are primarily a function of the harmonic force constant — the anharmonicity is difficult to see directly from this picture.

8.5.1 Offsets in Near Neighbor Distances

As was done throughout the earlier sections of this chapter, it is interesting to compare the offset in impurity-host near-neighbor distance \( \Delta R_{\text{off}} \) found by XAFS with the known change in lattice constant caused by the addition of these impurities. Table 8.6 lists the values for \( \Delta R_{\text{off}} \) found by XAFS along with the average change in near-neighbor distance from x-ray diffraction [104]. The sign of the distortions measured by XAFS are all seen to agree with the signs of the distortions found by diffraction. The
Table 8.5: One-Dimensional Anharmonic Force Constants for Ag-based alloys. Listed are values of $\Delta R_{\text{off}}$, the offset in nominal near neighbor distance (relative to 2.892 Å), and the force constants $a$, $b$, and $c$ for each of the measured interatomic bonds in the Ag-based alloys.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta R_{\text{off}}$ (Å)</th>
<th>$a$ (eV/Å$^2$)</th>
<th>$b$ (eV/Å$^3$)</th>
<th>$c$ (eV/Å$^4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Ag (pure)</td>
<td>-0.004 (01)</td>
<td>2.92 (06)</td>
<td>-1.27 (18)</td>
<td>1.1 (0.5)</td>
</tr>
<tr>
<td>Ga-Ag (5%)</td>
<td>-0.039 (02)</td>
<td>1.66 (04)</td>
<td>-0.61 (04)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>Ga-Ag (2.5%)</td>
<td>-0.030 (04)</td>
<td>1.60 (06)</td>
<td>-0.64 (06)</td>
<td>0.7 (0.1)</td>
</tr>
<tr>
<td>Sn-Ag (5%)</td>
<td>+0.060 (10)</td>
<td>2.52 (18)</td>
<td>-0.91 (46)</td>
<td>0.0 (1.6)</td>
</tr>
<tr>
<td>Au-Ag (5%)</td>
<td>-0.020 (02)</td>
<td>3.26 (07)</td>
<td>-1.57 (07)</td>
<td>1.4 (0.4)</td>
</tr>
</tbody>
</table>

Figure 8.20: Interatomic Potentials $\psi(R)$ for the measured Ag-based alloys. Results are shown for pure Ag (Δ), 5% Ga in Ag (○), 2.5% Ga in Ag (+), 5% Sn in Ag (×), and 5% Au in Ag (□). Estimated uncertainties are comparable to the symbol size.
Table 8.6: Comparison of $\Delta R_{\text{off}}$ as measured by XAFS and the average change in near-neighbor distance as determined by diffraction for impurities in Ag. The values listed for $\Delta R_{\text{ave}}$ were calculated from change in lattice parameters from Ref. [104]. The fourth column lists the ratio of the two different measures of $\Delta R$, and the fifth lists this ratio times the nominal impurity concentration. Uncertainties for $\Delta R_{\text{ave}}$ from diffraction are not known, but are taken to be much smaller than those of $\Delta R_{\text{off}}$ from XAFS.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\Delta R_{\text{off}}$ (Å)</th>
<th>$\Delta R_{\text{ave}}$ (Å)</th>
<th>$\Delta R_{\text{off}}/\Delta R_{\text{ave}}$</th>
<th>$x\Delta R_{\text{off}}/\Delta R_{\text{ave}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-Ag (5%)</td>
<td>$-0.039$ (02)</td>
<td>$-0.0025$</td>
<td>16(1)</td>
<td>0.80 (05)</td>
</tr>
<tr>
<td>Ga-Ag (2.5%)</td>
<td>$-0.030$ (04)</td>
<td>$-0.0012$</td>
<td>25(3)</td>
<td>0.63 (08)</td>
</tr>
<tr>
<td>Sn-Ag (5%)</td>
<td>$+0.060$ (10)</td>
<td>$+0.0124$</td>
<td>5(1)</td>
<td>0.25 (05)</td>
</tr>
<tr>
<td>Au-Ag (5%)</td>
<td>$-0.020$ (02)</td>
<td>$-0.0008$</td>
<td>26(3)</td>
<td>1.3 (0.2)</td>
</tr>
</tbody>
</table>

Magnitudes of distortions around the near-neighbors are also seen to be considerably larger ($\sim 10$ times larger) than the average distortions of the lattices.

By multiplying the ratio of the XAFS $\Delta R_{\text{off}}$ to the average $\Delta R$ from diffraction by the impurity concentration, a number near unity is found for all four of the impurities in Ag. A result of unity for this scaled ratio would indicate that all of the lattice distortion in the alloy was in the impurity-host distance. While the uncertainties in the values of $x\Delta R_{\text{off}}/\Delta R_{\text{aver}}$ are large, the Ga impurities appear to take up most of the distortion in the Ga-Ag alloy, so that the Ag-Ag distances in this alloy would be essentially the same as in pure Ag. The Sn impurities are seen to not make up most of the lattice distortion, so that there must be significant contraction of some of the Ag-Ag distances as well. Finally, $\Delta R_{\text{off}}$ for Au-Ag overestimates the contraction of the lattice, suggesting that some of the Ag-Ag distances must expand slightly.

As mentioned in section 8.1, the results here for contractions of near-neighbor distances around impurities that are far in excess of the average contraction of the lattice confirm more comprehensive XAFS studies on this topic. Recently, a large study by Scheuer and Lengeler [47], measured the distortions in near-neighbor distance caused by many different substitutional impurities in both fcc and bcc elemental metals. They found systematic variations in the offsets of the impurity-host distances as a function of location of the impurity on the Periodic Table. They also compared their XAFS measurements to a few different phenomenological descriptions using elastic theory [109, 110]. These simple theories were found to give reasonably good qual-
Figure 8.21: Mean-square-displacement $\sigma^2$ of the various near-neighbor bonds in Ag-based alloys as functions of temperature. Shown are results for pure Ag ($\triangle$), 5% Ga in Ag ($\diamond$), 2.5% Ga in Ag (+), 5% Sn in Ag ($\times$), and 5% Au in Ag ($\square$). Uncertainties for the pure Ag and Au-Ag data are smaller than the symbol size.

Itative agreement with the observed contraction or expansion of the impurity-host distances.

8.5.2 $\sigma^2$ and the Lindemann Law for Melting

Next, we turn our attention to the mean-square-displacement $\sigma^2$ for the different systems as a function of temperature, shown in Fig. 8.21. There is a striking relationship between the temperature-dependence of $\sigma^2$ and the effect of the impurity on the bulk melting temperature of pure Ag. Au impurities raise the melting temperature of Ag, and $\sigma^2$ for the Au-Ag bond (shown with $\square$ in Fig. 8.21) are seen to be always lower than those of pure Ag (shown with $\triangle$). Ga impurities (shown with $\diamond$ for the 5% alloy and + for the 2.5% alloy) lower the melting temperature of Ag and have $\sigma^2$ that are well above those of pure Ag (the results for the two concentrations lie nearly on top of one another). Sn impurities lower the melting temperature of pure Ag, and the $\sigma^2$ of the Sn-Ag bonds ($\times$) are also consistently above those of pure Ag.

These results for $\sigma^2$ for the impurity-host bonds demonstrate that those impurities which lower the melting temperature of the host solid have larger thermal disorder in the impurity-host bonds, while those impurities which raise the melting temperature
of the host have smaller thermal disorder in the impurity-host bonds. This suggests that the Lindemann model of melting by vibrational instabilities of the solid may be an adequate description of how impurities change the melting behavior of bulk materials.

The standard description of the Lindemann criterion [5] for melting is that the crystal will melt when the amplitude of the thermal vibrations is some fraction of the interatomic distance. Based on lattice dynamics calculations [111], this fraction has been estimated as \( \sim 7\% \) for fcc metals such as Ag. The thermal vibrations considered in these treatments are those around the lattice site, as seen by diffraction, and not those in the bond length, as seen by XAFS. If the temperature dependence of \( \sigma^2 \) found by XAFS for pure Ag is extrapolated to its melting temperature, 1234 K, we get \( \frac{\sigma_{\text{Ag}}^2}{\sigma_{\text{Ag}}^2}(T_m) = 0.039 \pm 0.003 \text{ Å}^2 \). This gives a Lindemann fraction of \( \delta_L = \sigma / R \approx 0.068 \) for the ratio of disorder in bond length to the bond length itself. This is quite similar to the fraction found using the results of Stern, Liviš, and Zhang [39] for melted Pb. They measured \( \sigma_{\text{Pb-Pb}}^2(T_m) \approx 0.050 \text{ Å}^2 \) in both the solid and liquid at the melting temperature. With a near-neighbor distance of 3.50 Å for Pb, this gives \( \delta_L = \sigma / R \approx 0.064 \). The result for pure Au will be shown in chapter 9 to give \( \delta_L = \sigma / R \approx 0.073 \), which is fairly close to the value for pure Ag. Since \( \sigma \) has different meanings for XAFS and lattice dynamics, it is probably only coincidental that the two descriptions give similar Lindemann fractions.

To test whether or not the thermal vibrations of the impurity-host bond are large enough to drive the change in melting temperature, we can investigate the “average” \( \sigma^2 \) for a bond in each of the alloys and compare the temperature at which this average \( \sigma^2 \) will equal \( \frac{\sigma_{\text{Ag}}^2}{\sigma_{\text{Ag}}^2}(T_m) \). We can evaluate the average \( \sigma^2 \) for an alloy (with the impurity labeled as X below) in a simplistic way as

\[
\langle \sigma^2(T) \rangle = x_X \sigma_{\text{Ag}}^2(T) + (1 - x_X) \sigma_{\text{Ag}}^2(T),
\]

and then predict the melting temperature of the alloy as the temperature \( T \) at which \( \langle \sigma^2(T) \rangle = \sigma_{\text{Ag}}^2(T_m) \). Keeping only the leading order of \( T \) (so that \( \sigma^2 = k_B T/a \)) leads to

\[
\Delta T_m = T - T_m = T_m \left( 1 - \frac{a_{\text{Ag}} - a_X}{a_{\text{Ag}} - a_X} \right)
\]

This gives a simple prediction for the change in melting temperature of a pure material by adding an impurity X with concentration \( x_X \) into a host of pure host with melting temperature \( T_m \). The above equation is trivially generalized to any host material. This simple formula and the force constants measured by XAFS gives the
Table 8.7: Predicted values for $\Delta T_m$ by the addition of impurities into pure Ag using Eq. (8.2) and the results of XAFS analysis. For comparison, the observed values of $\Delta T_m$ are listed for both the solidus (at which the solid begins to melt, giving a more impurity-rich liquid and a purer solid if the melting temperature is lowered) and the liquidus (at which the liquid begins to freeze, giving a more impurity-rich liquid and a purer solid if the melting temperature is lowered). Observed numbers are taken from Hansen [1]. Uncertainties for all these numbers are probably $\sim 10$ K.

<table>
<thead>
<tr>
<th>Bond and Concentration</th>
<th>Predicted $\Delta T_m$ (K)</th>
<th>Liquidus $\Delta T_m$ (K)</th>
<th>Solidus $\Delta T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga-Ag (5%)</td>
<td>-47</td>
<td>-50</td>
<td>-100</td>
</tr>
<tr>
<td>Ga-Ag (2.5%)</td>
<td>-20</td>
<td>-25</td>
<td>-50</td>
</tr>
<tr>
<td>Sn-Ag (5%)</td>
<td>-12</td>
<td>-30</td>
<td>-80</td>
</tr>
<tr>
<td>Au-Ag (5%)</td>
<td>+7</td>
<td>+10</td>
<td>+5</td>
</tr>
</tbody>
</table>

results shown in Table 8.7. Also listed there are estimates of the observed melting temperatures for the measured systems, taken from the binary phase diagrams [1]. Observed values for both the liquidus and solidus melting lines are given$^3$.

Though simplistic and crude, the results of the comparison in Table 8.7 are compelling. The general finding is that the predicted melting temperature is quite close to the liquidus, and not consistent with the solidus. The implication is that the solid alloy becomes as vibrationally disordered as the pure Ag melt at a temperature near the liquidus line. But the vibrations are not by themselves sufficient to make the solid alloy unstable at the solidus line. The fact that the solid actually melts at the lower temperature of the solidus may then be explained by the more usual thermodynamic arguments, which derive from the equality of the free energy of the solid and liquid at melting, and include the change of the entropy of mixing at melting (since the impurity concentration in the liquid is different than that of the solid) and the change in configurational entropy at melting. One such thermodynamic description for the

$^3$ As explained in many introductory thermodynamic texts, the solidus is the line at which the solid begins to melt and the liquidus is the line at which the liquid begins to freeze. In a system in which the impurity lowers the melting temperature, the solid will melt at the solidus into an impurity-rich liquid, leaving a more pure solid. The liquid will freeze at the liquidus into a more pure solid, leaving an impurity-rich liquid. A detailed explanation of this is given in Ref. [2].
change in melting by the addition of a small amount of an impurity is given as [2]
\[ \Delta T_m = k_B T_m^2 \frac{(c_s - c_l)}{q} \] (8.3)
where \( \Delta T_m \), the change in melting temperature, is given in terms of \( q, s \) the latent
heat of melting the pure material, and \( c_s \) and \( c_l \), the concentration of the impurity
in the solid and liquid, respectively. The thermodynamic arguments that lead to this
formula do not consider which atoms make up the alloy, but do give a reasonably
good theoretical framework to the change in melting temperature by adding a dilute
impurity for a pure host. If the liquidus line is known by other means (such as
the XAFS results here), then the solidus line should be determined quite accurately
from simple thermodynamics such as given in Eq. (8.3). The combination of these
thermodynamic considerations and the experimental findings here may give important
insight to the nature of impurity-induced melting.

Finally, the \( \sigma^2 \) for the Ga-Ag bonds show an interesting contrast to the Hg-Pb
bonds measured by Stern and Zhang [50]. They found that \( \sigma_{Hg-Pb}^2 \) rose much more
quickly with temperature than did the \( \sigma_{Pb-Pb}^2 \). But they also found that \( \sigma_{Hg-Pb}^2 \)
did not exceed \( \sigma_{Pb-Pb}^2(T_m) \). They interpreted this as meaning that the Hg-Pb bond
“melted” at the temperature (well below the bulk melting temperature) at which the
\( \sigma_{Hg-Pb}^2 \) equaled the \( \sigma_{Pb-Pb}^2(T_m) \). For the Ga-Ag bond, \( \sigma_{Ga-Ag}^2 \) is also seen to rise
much more quickly with temperature than \( \sigma_{Ag-Ag}^2 \) of the pure host. But unlike the
Hg-Pb bond, \( \sigma_{Ga-Ag}^2 \) is also seen to exceed \( \sigma_{Ag-Ag}^2(T_m) \) at \( \sim 750 \) K, and to continue
to rise well above \( \sigma_{Ag-Ag}^2(T_m) \) (which, was estimated above as \( \sim 0.039 \) Å²). The
interpretation here is that the Ga-Ag bond does not pre-melt in the same way that
the Hg-Pb bond was seen to do.

8.5.3 Thermodynamic Properties for Impurity-Host Bonds

We now look at the remaining thermodynamic parameters calculated for the bonds in
the Ag-based alloys from the XAFS measurements of the anharmonic force constants.
These parameters have been discussed in chapter 5 and throughout this chapter, and
the results are summarized in Table 8.8. Based on the reasonably good agreement
between all values obtained from XAFS measurements for thermodynamic parameters
of pure Ag with the known bulk values, the idea of using XAFS to measure these
properties is shown to be reliable. It also seems that the force constants (at least \( a \)
and \( b \)) that give the XAFS cumulants are measured reasonably well, since all the ther-
modynamic parameters use different algebraic combinations of these force constants.
Table 8.8: Thermodynamic Parameters for Ag-based alloys. Listed are values of the linear coefficient of thermal expansion $\alpha$, the Grüneisen parameter $\gamma$, and bulk modulus $K$ for each of the measured interatomic bonds in the Ag-based alloys. The first row lists the known values for pure Ag from measurements of bulk properties.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$\alpha$ (10$^{-6}$)</th>
<th>$\theta_E$ (K)</th>
<th>$\gamma$</th>
<th>$K$ (eV/Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Ag (Bulk)</td>
<td>19.2 (1.0)</td>
<td>175</td>
<td>2.5</td>
<td>0.65</td>
</tr>
<tr>
<td>Ag-Ag (XAFS)</td>
<td>17.0 (2.0)</td>
<td>174 (2)</td>
<td>2.57 (0.17)</td>
<td>0.79 (0.11)</td>
</tr>
<tr>
<td>Ga-Ag (5%)</td>
<td>26.4 (1.7)</td>
<td>148 (2)</td>
<td>2.91 (0.18)</td>
<td>0.59 (0.05)</td>
</tr>
<tr>
<td>Ga-Ag (2.5%)</td>
<td>29.3 (2.7)</td>
<td>146 (3)</td>
<td>2.71 (0.16)</td>
<td>0.49 (0.05)</td>
</tr>
<tr>
<td>Sn-Ag (5%)</td>
<td>16.6 (6.6)</td>
<td>158 (6)</td>
<td>2.84 (1.15)</td>
<td>0.84 (0.48)</td>
</tr>
<tr>
<td>Au-Ag (5%)</td>
<td>16.7 (0.9)</td>
<td>162 (2)</td>
<td>2.47 (0.05)</td>
<td>0.79 (0.05)</td>
</tr>
</tbody>
</table>

Bulk thermodynamic properties for the alloys have not been found in the literature, and the direct comparison of the measured impurity-host bond parameters with bulk properties of the alloy would not be easy anyway. The values listed in Table 8.8 are taken as results of the XAFS measurements that characterize the impurity-host bond and which have no directly comparable bulk properties available.

The anharmonic force constants can also be used to calculate the temperature-dependent thermodynamic parameters such as the heat capacity and entropy. We start with the heat capacity. Using Eq. (5.15), we obtain the values shown in Fig. 8.22. Since these calculations are done in one-dimension, the classical harmonic oscillator term would be $k_B$. Deviations from this value are seen to be small. Though it is seen that the Ga-Ag bonds show the smallest heat capacity, the effect of this on the heat capacity of the whole solid will be quite small, since so few (~5%) of the bonds are Ga-Ag bonds.

Figure 8.23 shows the vibrational entropy of the impurity-host bonds, as calculated using Eq. (5.14). The most striking feature of the temperature dependence of the vibrational how similar they are. Despite the dependence of the vibrational entropy on the force constants and the reduced mass of the bond, which vary greatly between these systems, there is little net change in the vibrational entropy of the interatomic bonds. Though the differences are small, it can be seen that $S_{vib}$ is lowest for the Ag-Ag bonds, next lowest for the Au-Ag bonds, and highest for the Ga-Ag and Sn-Ag bonds.

For comparison, the entropy of mixing for a 95% – 5% mixture is $S_{mix} \approx 0.2 \, k_B$. 
Figure 8.22: Vibrational Heat Capacity $C_{\text{vib}}$ of Near-Neighbor Bonds in Ag-based alloys as functions of temperature. Shown are results for pure Ag ($\Delta$), 5% Ga in Ag ($\diamond$), 2.5% Ga in Ag (+), 5% Sn in Ag ($\times$), and 5% Au in Ag ($\square$). Estimated uncertainties are comparable to the symbol size.

Though considerably less than the vibrational entropy at reasonably high temperatures, the entropy of mixing is larger than the difference of any two of the vibrational entropies shown. It's not clear what implication this has for the influence of impurities on melting, since it is the change in entropy between the liquid and solid that is most relevant to melting. It is conceivable that the change in the vibrational entropy at melting is comparable to the change in the entropy of mixing at melting. There are additional terms to the change in entropy at melting (such as the change in positional or configurational entropy) which may also be important.

Combining the results here for $S_{\text{vib}}$ and those of section 8.5.2 (which suggested that vibrational melting would occur at the liquidus line of the binary phase diagram) indicate that the vibrations of the impurity-host bonds are important in changing the melting temperature, but that the changes in the vibrational entropy are quite small. This seems to suggest that the harmonic force constant ($a$) is a better predictor of the change in melting temperature, and that using the reduced mass of the bond (as when calculating $\theta_E$ or $S_{\text{vib}}$) confuses the interpretation. To fully explain why impurities change the melting temperature, a more complete thermodynamic description of the system is needed. By far the most important consideration left out of the treatment...
Figure 8.23: Vibrational Entropy $S_{\text{vib}}$ of Near-Neighbor Bonds in Ag-based alloys as functions of temperature. Shown are results for pure Ag ($\triangle$), 5% Ga in Ag ($\diamond$), 2.5% Ga in Ag ($+$), 5% Sn in Ag ($\times$), and 5% Au in Ag ($\Box$). Estimated uncertainties are comparable to the symbol size.

Here is the nature of interatomic bonds in the liquid.