Atomic Displacements in Alloys

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The atoms in an alloy move away from their ideal lattice sites because of thermal vibrations and the static displacements that are due to the difference in atomic sizes. These vibrations and displacements are simulated using molecular dynamics and potentials obtained from the embedded atom method. The thermal vibrations of pure copper are shown. The static displacements for copper-gold, copper-palladium, and copper-aluminum are calculated and displayed.

EVEN with the petaflop computers that are soon to come on line, completely first principles calculations of static and thermal vibrations in alloys are out of the question. There are many approximations that can speed up the calculations while introducing errors that may be acceptable. The most common approximation is to ignore the thermal and zero-point motion of the atoms and calculate the total energy of a finite cluster of atoms at specified positions \( R_i \) using the density functional theory (DFT) and the local density approximation (LDA).[1] The configuration of the positions that corresponds to the minimum energy gives the static displacements. As we will demonstrate in more detail, the results obtained with this approximation are contradictory and do not agree with experiment.

We choose to take a different path and calculate the static and thermal displacements in alloys quasi-classically, by which we mean that Newton’s laws are used to describe the positions of the atoms in time but the interatomic potentials are obtained from the embedded atom method (EAM)[2] that has a quantum mechanical basis. The EAM potentials are obtained from a DFT energy expression, and they have a volume-dependent electron gas term in addition to the interatomic interactions. The EAM potential contains parameters that are adjusted to give the best fit to the experimental values for elastic constants, vacancy formation energies, lattice constants, sublimation energies, bulk modulus, and the equations of state of the pure metals. Some remaining ambiguities can be removed by fitting to the dilute limits of the heats of solution of binary alloys.

In a static solid with no thermal or zero-point motions, the only energy in the model is the potential energy \( V(R_1, R_2, R_3, \ldots R_N) \). The force on the \( i \)th atom is given by taking the gradient of the potential with respect to the coordinates \( R_i \) of that particle:

\[
\mathbf{F}_i = -\nabla_i V(R_1, R_2, R_3, \ldots R_N) \quad [1]
\]

In an earlier calculation,[3] EAM forces have been used in a conjugate gradient program to calculate the positions of the atoms by minimizing the potential energy.

We note that a calculation of atomic positions in a hypothetical static solid is not very useful because disentangling the thermal and static displacements is always a necessary step in the analysis of experimental data. The positions of the atoms at any time \( t \), \( R_i(t) \), in a solid at temperature \( T \) are given by a molecular dynamics (MD) calculation. The forces at any time \( t \) can be found from Eq. [4] using the instantaneous positions \( R_i(t) \). The MD calculations are normally used to study disordered states of condensed matter such as liquids and defects in solids. It has been observed that MD can be used to study the thermal motion of atoms about their lattice sites in a crystal.[5] If the calculation is initiated with the atoms in the correct crystal structure, they do not diffuse away from their sites as long as the model contains no vacancies and the temperature remains below the melting point. In the current study, this approach is extended to alloys where the difference in atomic sizes leads to the additional feature that there are static displacements from the lattice sites. The parameters in the EAM potentials used in this study differ from the ones in the literature, because the atomic size is given the highest weight in the fitting procedure. Checks were made to ensure that the other properties of the pure crystals are still reproduced within acceptable limits.[5]

Further checks were made to test the reliability of our potentials in alloy calculations. For example, lattice constants were calculated as a function of temperature and concentration. Also, the melting points of the alloys were calculated. Comparisons of these calculations with experiment provide assurance that our MD potentials give an accurate description of the alloys. Details about the calculations will be described elsewhere.

The time average of the positions of the atoms calculated with MD is

\[
R_i = \frac{1}{\tau} \int_0^\tau R_i(t) \, dt \quad [2]
\]

where \( \tau \) is a sufficiently long time. These are the average atomic positions that are obtained from the analysis of X-ray or extended X-ray absorption fine structure (EXAFS) data and are used to calculate the static displacements. The mean square displacements of the atoms,

\[
\langle (\Delta R_i)^2 \rangle = \frac{1}{\tau} \int_0^\tau [R_i(t) - \bar{R}_i]^2 \, dt \quad [3]
\]

are the thermal displacements that lead to diffuse scattering.

The diffuse scattering intensities calculated for pure copper using the mean square displacements defined in Eq. [6]...
at temperatures 295 and 723 K along the direction \((h00)\) in \(k\)-space are compared with the X-ray diffraction measurements in Figure 1. The essentially infinite intensities at the Bragg peaks have been subtracted out, so the thermal diffuse scattering shown is only due to the vibration of the atoms about their lattice sites. The experimental values shown in the figure were measured at the National Synchrotron Light Source (Brookhaven, NY), using 13.0 keV X-rays.\(^6\) Because the MD data set contains the \(R_j(t)\) for alloys as well as pure metals, it is no harder to calculate the thermal diffuse scattering intensities for alloys, but there are no reliable experimental data to compare with at this time.

The static displacements in, e.g., a copper-gold alloy are characterized by comparing the separation of Cu-Cu nearest-neighbor pairs, \(d_{\text{CuCu}}\), Au-Au nearest-neighbor pairs, \(d_{\text{AuAu}}\), and Cu-Au nearest-neighbor pairs, \(d_{\text{CuAu}}\). These distances are based on the time averaged positions \(\bar{R}_i\) defined in Eq. [5]. In a 32,000 atom supercell representing a Cu\(_{0.5}\)Au\(_{0.5}\) alloy, there are 48,000 Au-Au pairs, 96,000 Cu-Au pairs, and 48,000 Cu-Cu pairs. The supercell is periodically reproduced in space to avoid surface effects. Each pair has a slightly different nearest-neighbor separation \(\bar{R}_i - \bar{R}_j\), so \(d_{\text{CuCu}}, d_{\text{AuAu}},\) and \(d_{\text{CuAu}}\) are actually the mean of the separations. If there were no static displacements, the pair separations would be the same for the different types of pairs.

The most straightforward way to measure \(d_{\text{AuAu}}, d_{\text{CuAu}},\) and \(d_{\text{CuCu}}\) is with X-ray absorption fine structure (XAFS) spectroscopy. The techniques of XAFS spectroscopy are well described in many books and review articles.\(^7\) One XAFS study has been made of Cu\(_{1-x}\)Au\(_x\) alloys that covers the entire range of atomic fractions \(0.0 \leq x \leq 1.0.\(^8,9\)

The data from that study are compared in Figure 2 with the predictions of our MD calculations using a 32,000 atom supercell. The temperature in the MD calculations was set at 80 K, which is close to the temperature at which the experiments were done. We do not show the error bars on the experimental data, but it is clear from the irregular variation with \(x\) of those data that they are large. The experimental values for pure Cu and Au are from ordinary X-ray measurements, and the agreement with our MD calculations was predetermined. The excellent agreement between the MD calculations and experiment for finite concentrations is meaningful, however, because no information about the alloys was built into the choice of EAM parameters.

A feature of the experimental results that has attracted a great deal of interest is that there is an atomic fraction of gold \(X\) beyond which \(d_{\text{CuCu}} > d_{\text{CuAu}}\). If one pictures the insertion of a larger atom into a matrix of smaller atoms, the existence of this crossover seems to violate physical intuition. It simply means that the volume per atom is increasing faster than the average repulsion of the Cu atoms by the Au atoms. It is difficult to see in the figure, but the MD calculations give the crossover at exactly the same concentration as experiment, \(X = 0.86\).

One of the frequently quoted successes of the DFT is the calculation of lattice constants. There are two approximations to the DFT that are in wide use, the original LDA\(^1\) and the generalized gradient approximation (GGA).\(^10\) The technical descriptions of these approximations are of no interest in the present context, but the nearest-neighbor distances they predict for pure Cu and Au are shown in Figure 2. The calculations have been done correctly with relativistic codes and no shape dependence to the

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**Fig. 1**—A graph of the temperature diffuse scattering for pure copper along the direction \((h00)\) in \(k\)-space. The experimental intensities for the temperature 295 K are shown by circles and for 723 K by squares. They are from the unpublished communication quoted in Ref. 6. The intensities calculated with MD are shown by the solid and dotted lines. The units of the intensities are arbitrary, and \(h\) is in units of \(2\pi\) over the lattice constant.

**Fig. 2**—The Cu-Cu, Cu-Au, and Au-Au pair separations calculated with the EAM are plotted as a function of composition. They are shown with filled diamonds, squares, and circles, respectively. The data measured with XAFS are indicated by the large open markers. The triangles show the results of LDA and GGA calculations.