Analysis of Short-Range Order in Cu₃Au using X-ray Pair Distribution Functions

L.R. Owen^{a,b}, H.Y. Playford^{b,*}, H.J. Stone^a, M.G. Tucker^c

^a*Department of Materials Science and Metallurgy, University of Cambridge, CB3 0FS, UK*

^b*ISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0QX, UK*

^c*Spallation Neutron Source, One Bethel Valley Road, Oak Ridge, Tennessee, USA*

Abstract

Cu₃Au is often cited as a case example of a metallic system exhibiting both short-range order in the solid solution phase and a long-range order-disorder transition. In this work, X-ray total scattering data obtained from the in situ heating of a gas-atomised powder sample of Cu₃Au are used to demonstrate the suitability of total scattering, in conjunction with large-box modelling, for the analysis of short-range order in alloys. The existence of an ordering transition at c. 400° is confirmed, and the development of short-range order reminiscent of the L1₂ long-range ordered structure is observed prior to this transition. Furthermore, it is found that a degree of short-range order is present even in quenched samples (usually assumed to be completely random) which throws into question the identification of short-range order in previous ex situ studies. It is demonstrated that total scattering can be used successfully to identify the type and degree of ordering, differences in the bond length distributions in the first coordination shell and to suggest a likely mechanism for the formation of order in the system.

Keywords: Atomic ordering, Diffraction, Pair correlation function, Short-range order, Short-range ordering

1. Introduction and Background

The arrangement of atoms in solid-solution alloys is commonly considered to be random across all length scales. However, owing to unexplained physical phenomena such as increased strengthening, thermodynamic discontinuities and electrical resistivity effects, it has been argued that this model is oversimplified and that these effects are attributable to short-range ordering of the atomic species. Conventional crystallographic analysis, using Bragg scattering [1], provides information only on the long-range average structure. However, the total

*Corresponding author

Email address: helen.playford@stfc.ac.uk (H.Y. Playford)

scattering technique, in which both Bragg and diffuse scattering are analysed simultaneously, can overcome this limitation and determine the short-range order present in the system. To facilitate the analysis of such data, methods based on the reverse Monte-Carlo technique [2] have been developed and used to provide greater insight into a variety of materials [3]. However, to date, total scattering has rarely been applied to the study of short-range order (SRO) in alloys. In a previous paper [4], a method by which SRO in metal alloys can be determined from total scattering data was proposed. In this paper, X-ray total scattering data from Cu_3Au have been used to demonstrate this analysis in action.

The Cu-Au alloy system is often used as a case example of ordering transitions in metal alloys and of short-range order in a solid solution. At higher temperatures, a complete solid solution is observed across the full compositional range, which has the $\text{A1}^\dagger$ face centred cubic (*fcc*) structure. Below a critical temperature, T_c , the Cu-Au alloys are known to form two long-range ordered cubic structures: L1_0 (CuAu , $T_c \approx 410^\circ\text{C}$ [5]) and L1_2 (Cu_3Au , $T_c \approx 390^\circ\text{C}$ and CuAu_3 , $T_c \approx 240^\circ\text{C}$ [5]).

Analysis of ordering in Cu_3Au was first carried out in the seminal work of Cowley [6]. Since then, it has been used as a benchmark for comparison of analysis techniques due to the presence of diffuse scattering both pre- and post-ordering. Indeed, Clapp [7] used the Cu-Au system to demonstrate the use of probabilistic analysis and his description of short-range ordering in a material.

In a study by Borie [8] a change in the diffuse scattering close to the (300) reflection of a sample of Cu_3Au was reported when the sample was quenched from above 600°C , compared with quenching from below this temperature. However, it was also noted that this may not simply indicate the presence of a greater degree of SRO above 600°C , as the effect of quenching on the SRO was not fully understood. A proposed explanation for the change at 600°C was the existence of micro-domains in the region $T_c < T < 600^\circ\text{C}$.

Walker and Keating [9] re-evaluated the original results of Cowley in order to take into account developments in diffuse scattering theory to include thermal vibrations and static displacements. Largely these effects made little difference to the calculated α -parameters [6, 10], except for the two nearest neighbour terms. Similarly Moss [11] re-evaluated the original Cowley data extending the result to a calculation of the α -parameters for the first ten co-ordination rings of the system. Moss and Clapp [12] carried out an analysis on CuAu_3 and Cu_3Au using their thermodynamic approach to calculate the pair-potentials from the extracted α -parameters.

A more systematic X-ray diffraction study of Cu_3Au across the temperature range $T_c < T < 930^\circ\text{C}$ was carried out on a single crystal using a lab based Cu-K α source by Bardhan and Cohen [13]. Close to T_c , diffuse scattering was observed at the $[1 \frac{1}{2} 0]$ position, which was believed to indicate the presence of domains of both the D0_{22} and L1_2 structures. As the temperature was increased the observed D0_{22} pattern disappeared, whilst a $[\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ diffuse maximum be-

[†]Strukturbericht notation

came apparent, not previously reported in the literature. Calculation of the α -parameters agreed well with previous results. Computer simulations based on the diffuse data gathered suggested that the specific heat anomaly present at 600°C is due to the loss of D0₂₂ micro-domains in the alloy; whilst that at 850°C is due to the development of L1₁ regions. The consensus from these studies is that the ordering transition is preceded by a region ($T_c < T < 600^\circ\text{C}$) in which SRO is observed, related to either the L1₂ and D0₂₂ structures, with the system becoming a solid solution above $\sim 600^\circ\text{C}$.

Whilst most of these studies were based on traditional single crystal experiments, more recently Proffen et al. [14] recognised the potential of total scattering for the analysis of ordering in alloy systems. X-ray total scattering data were collected from two samples of polycrystalline Cu₃Au manufactured by grinding a cast ingot, one ordered and one disordered. However, no data was obtained in their study on the intermediate ordering states. From fitting of these data with a reverse Monte Carlo (RMC) refinement, implemented within the DISCUS software [15], α -parameters for the completely ordered and disordered systems were calculated.

In this current work, a systematic measurement of the short-range order in Cu₃Au has been made using *in situ* X-ray total scattering. Analysis of these data using the RMC method represents the first application of the method outlined in our previous theoretical work [4] to real experimental data and demonstrates the potential of total scattering to provide a better understanding of ordering occurring in metallic systems beyond analyses based on Warren Cowley α -parameters alone.

2. Background theory

2.1. Total scattering and pair distribution functions (PDFs)

The total scattering function, $F(Q)$, is related to the total differential cross section (σ) by:

$$\frac{1}{N} \frac{d\sigma}{d\Omega} = F(Q) + \sum_{i=1}^n c_i \bar{b}_i^2 \quad (1)$$

where Ω is the solid angle into which scattering occurs, c_i the concentration and $\bar{b}_i$ the atomic scattering length (or form factor) of species i . N is the total number of atoms in the system. The PDF is a Fourier transform of the $F(Q)$ given by the equation:

$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} dQ \quad (2)$$

where ρ_0 is the average density of the structure, Q the magnitude of the scattering vector and r the real space interatomic distances. The PDF is frequently used owing to the intuitive nature of the real space representation. By definition

the PDF is a weighted histogram of the interatomic distances in a system and is defined by:

$$G(r) = \sum_{i,j} c_i c_j \bar{b}_i \bar{b}_j (g_{ij}(r) - 1) \quad (3)$$

where $g_{ij}(r)$ terms are the partial pair distribution functions, c_i & c_j and $\bar{b}_i$ & $\bar{b}_j$ are the concentrations and scattering lengths (or form factors) of the atomic species i and j respectively. Alternative representations of the PDF are possible such as the $T(r)$:

$$T(r) = 4\pi r \rho_0 \left[G(r) + \left(\sum_{i=1}^n c_i \bar{b}_i^2 \right)^2 \right] \quad (4)$$

For more information about this formalism and alternative representations of the PDF, see Keen [16].

2.2. Descriptors of short-range order

To provide a quantification of and description of SRO present in a large box model, the following descriptors may be employed. The use of the descriptors for such analysis is described in detail in our previous work [4].

Warren-Cowley parameters

The Warren-Cowley α -parameters [6, 10] provide a measure of order in a specific coordination shell, by comparing the observed concentration of an atom type to that predicted by the stoichiometry. They are defined as:

$$\alpha_{lmn}^{AB} = 1 - \frac{P_{lmn}^{AB}}{c_B} = 1 - \frac{P_{lmn}^{BA}}{c_A} \quad (5)$$

where P_{lmn}^{AB} is defined as the probability of finding a B atom at position $\vec{r}_{lmn} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$ (where $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ are lattice vectors, and l , m and n are fractional coordinates) from an origin placed on an A atom, and c_A and c_B are defined as the atomic fractions of A and B respectively in the alloy.

Clapp configuration enhancement factors

Clapp configurations [7] describe the 144 possible arrangements of two atom types across the twelve nearest neighbours in a *fcc* lattice. Each Clapp configuration is numbered and will be italicised in this text to avoid confusion (e.g. *C1*). A quantitative measure of the number of each Clapp configuration present in an atomistic model, relative to the random configuration, can be achieved through use of an enhancement factor β defined as:

$$\beta_a = \frac{n_a - \bar{n}_a}{\sigma_{n_a}} \quad (6)$$

where n_a is the observed number of configurations a existing in a refined box and $\bar{n}_a$ and σ_{n_a} are the expected number and standard deviation predicted from a random model. From this definition it follows that values of $|\beta_a| \leq 3$ are most likely due to random statistical fluctuations in the box, and therefore if $|\beta_a| \geq 3$ the configuration a can be considered truly enhanced (or reduced).

Figure 1: Temperature profile of the sample with time. Points marked with cross represent the total scattering datasets.

3. Experimental details

A powder sample of Cu_3Au (i.e. $\text{Cu-25at.\%Au}$) was produced by water atomisation and sieved to yield a particle size $< 45\mu\text{m}$ to ensure that a powder average would be obtained when the sample was illuminated by the X-ray beam. The powder was loaded into a 0.5 mm diameter silica glass capillary and placed on the I15 beamline at the Diamond Light Source Ltd, Didcot, UK. The instrument was set up to record diffraction data in transmission geometry with a Perkin-Elmer flat plate 1621EN detector, with a sample to detector distance of ~ 210 mm. This enabled scattering data to be acquired across an angular range from $2 < 2\theta < 42^\circ$. A CeO_2 sample was used for calibration of the sample to detector distance using a fixed energy $E = 75.534$ keV. Total scattering data were gathered of the ‘as-received’ sample at room temperature prior to heating. The sample was subsequently heated using a Cyberstar gas blower apparatus to 900°C . The system was stepped down in temperature in 100°C steps over a series of hours until ordering occurred and superlattice peaks appeared in the diffraction pattern. At each step, total scattering data were acquired. The system was then held at this temperature for a second hour to allow further ordering to occur. The temperature was then raised to 500°C and subsequently reduced in smaller 10°C increments in the region close to the critical temperature and the ordering transition. The temperature profile of the data with time is shown in Fig. 1.

The X-ray data were subsequently reduced and corrected using the DAWN software package [17]. Rietveld refinements [18] were carried out using the GSAS [19] software package. The total scattering data were processed and corrected for self-scattering and sample container scattering using GudrunX [20, 21], to yield total scattering functions. Subsequent Fourier transforms, to yield PDFs, were carried out using the StoG routine, distributed as part of the RMCProfile package [22], using a $Q_{\text{max}} = 26 \text{ \AA}^{-1}$. Neutron total scattering data of the as-received powdered Cu_3Au sample were also measured at room temperature on

the Polaris diffractometer at the ISIS Neutron and Muon Source, Didcot, UK. The data were corrected, normalised and collated using the Mantid software [23] and the total scattering functions processed using the GudrunN software [20].

4. Data processing and analysis

4.1. The RMC algorithm and data processing errors

The RMC fitting algorithm creates an atomistic model that best represents a group of input datasets. From an initial configuration, a series of random atom moves (translations and swaps) are made. Moves that improve the quality of the fit to the data are accepted automatically, whereas moves that reduce the quality of fit are subjected to an acceptance probability criterion. This allows a certain number of bad moves to be accepted, thereby reducing the chances of the refinement getting stuck in false minima. The algorithm can, therefore, make moves that improve the fit to the data, irrespective of physical sense. The extent to which unrealistic moves are accepted can be minimised by the introduction of physical constraints (e.g. minimum bond distances). However, data that contain errors from incorrect collection or processing methods will still be fitted by the algorithm and may result in configurations that reflect these processing artefacts rather than any real information contained within these data sets. It was, therefore, essential to consider such artefacts and ensure the data has been correctly processed, prior to fitting, to ensure the configurations were representative of the order in the system and not merely an artefact produced by incorrect handling of the data.

Instrument resolution function

A resolution function is used to describe the way that instrumental parameters affect the data. The function itself, which may consist of a complex mixture of exponentials, Gaussian and Lorentzian terms, is convoluted with every point in the gathered reciprocal space data. In its most simple and basic form this function may be approximated as a Gaussian function, with a Q -independent width. For X-ray synchrotron data acquired using a flat-plate detector, such as the one used in this experiment, this is a reasonable approximation. Consequently, the corresponding effect on the PDF will be a decay envelope of the form:

$$S(r) = \exp\left(\frac{-(\Delta Q)^2 r^2}{2}\right) \quad (7)$$

where ΔQ can be estimated from the observed full width half maximum of peaks in the total scattering function $F(Q)$. The $S(r)$ can be used to correct the PDF for the instrumental resolution. A subsequent reverse Fourier transform can be used to obtain a resolution corrected $F(Q)$. An equivalent result could also be obtained by convolving the original data set with a resolution function, however, this is more computationally expensive.

Incorrect lattice parameter measurements

Normally the lattice parameters used to generate the initial atomic model for the RMC refinement are obtained from the Rietveld analysis of the Bragg data. However, care is required as any inconsistencies in calibration during the processing of the Bragg and total scattering data are likely to compromise the integrity of the atomic model produced.

4.2. Simulation of data processing errors

To demonstrate the consequences of not accounting for the instrumental resolution function or errors in the lattice parameters, a series of atomic models were generated containing $20 \times 20 \times 20$ *fcc* unit-cells. Of the 32,000 atoms in the box, the atoms were randomly assigned as either copper or gold, in a ratio of 3:1, and randomly displaced from their idealised positions in a gaussian distribution using the Box-Muller method [24] to represent thermal displacements. For each of these boxes the theoretical X-ray PDF was calculated*.

To assess the effect of these potential data processing errors on atomistic models produced by RMC fitting, the calculated PDFs were artificially altered in the following ways:

- damping by multiplying by the scaling function $S(r)$ with $\Delta Q = 0.031 \text{ \AA}^{-1}$. This ΔQ value is representative of the instrumental broadening observed in the experimental data.
- offsetting the data by $0.02 \text{ \AA}$ (a typical histogram bin width), using the box used to generate the data as a starting configuration.

These PDFs, representative of different processing errors, were subsequently fitted using the atomistic models that had been used to generate the datasets. A third simulation was carried out using the calculated dataset, but fitting with an atomistic model with a lattice parameter 0.1% larger than that used to simulate the original data set, representative of an error in the third decimal place of the calculated lattice parameter. The theoretical dataset was also fitted using a starting model with all atoms on their idealised lattice sites to provide a reference. The simulations were run allowing both swaps and translations to occur in a ratio of 1:3. The data processing error datasets and the PDF fits before and after refinement are shown in Fig. 2. As can be observed, in spite of the deliberately introduced discrepancies between the datasets and boxes used in the fitting process, an excellent fit was obtained using the RMC algorithm.

*In the processing of X-ray total scattering data and calculation of the total scattering functions, it is common to use an average atomic form factor to account for the Q -dependence of the individual atomic form factors. This effectively approximates the system as a series of point scatterers, where the atoms have scattering coefficients proportional to the atomic number Z . Accordingly, both experimental and theoretical data presented in this paper have been handled in this way.

Figure 2: PDF $T(r)$ datasets and fits for runs with shifts in lattice parameter (both r dependant and independent). Circles indicate the data sets for fitting, black lines the RMC fit and the grey line the difference between the data set and the fit. (a) and (b) show the ‘instrumental resolution’ datasets with the calculated $T(r)$ before and after refinement respectively. (c) and (d) show the fitting with a box with a 0.1% change in the lattice parameter with the calculated $T(r)$ before and after refinement respectively. (e) and (f) show the data set with the systematic shift of $0.02\text{\AA}$ with the calculated $T(r)$ before and after refinement respectively

Figure 3: Output supercell boxes and versions collapsed back onto a single unit cell from RMC runs fitting data with different processing errors. Dark spheres represent gold atoms, light spheres copper atoms. (a) and (e) are from fitting to calculated data (with no errors) with an idealised random box. (b) and (f) are the outputs fitting a dataset damped by an instrumental resolution function $S(r)$ with $\Delta Q = 0.031 \text{ \AA}^{-1}$. (c) and (g) are the outputs from fitting a calculated dataset with a box with a 0.1% error in the lattice parameter. (d) and (h) are the outputs from fitting calculated data with a systematic shift in r of $0.02 \text{ \AA}$.

The atomistic models obtained from the fitting, along with these models collapsed back onto a single unit cell, are shown in Fig. 3. A region of deformation can be observed in the middle of the supercell in all three examples, with that resulting from the instrumental resolution effect, Fig. 3b, being particularly obvious. What is more striking, for the exponential decay fitting, is considering the result when the atoms were condensed back onto a single unit-cell, as shown in Fig. 3f. From Fig. 3f it is apparent that the distribution of the atoms in the supercell is no longer describing the expected ellipsoidal shape, but instead show regions of deformation. Such results are physically unrealistic and the presence of such offsite displacements in an RMCProfile output for a crystalline alloy system are likely to be indicative of incorrectly processed data. Some deformation of the thermal ellipsoid and offsite displacement can also be observed in the other processing errors, but they are less significant.

The Warren-Cowley α -parameters and Clapp configuration enhancement factors, calculated as described in our previous theoretical work [4], are shown in Fig. 4. Fitting the datasets, representative of the artificially applied processing errors, there is a large enhancement in the $C1$ and $C2$ configurations in all boxes, again with the exponential decay box showing a much larger effect. The $C1$ configuration describes atoms surrounded by atoms of the same type. This has not been observed in the Cu-Au system and indeed is shown through this case example to be an artefact of fitting to incorrectly processed data. There

Figure 4: Enhancement factors, β , and Warren Cowley parameters, α , for the boxes shown in Fig. 3. The enhancement factors for the different simulated data sets are (a) fitting ideal calculated data with a random box, (b) fitting a dataset damped by an instrumental resolution function $S(r)$ with $\Delta Q = 0.031 \text{ \AA}^{-1}$, (c) fitting a calculated dataset with a box with a 0.1% error in the lattice parameter, and (d) fitting calculated data with a systematic shift of 0.02 $\text{\AA}$. The dotted lines in these plots indicates the bounds between which random fluctuations in the box are expected. Panels (e) and (f) show the Warren-Cowley parameters for the outputs. The dashed line shows the predicted L12 structure and the dotted line the idealised random value. In (e) the black line indicates the results of fitting the unaltered dataset and the grey line the instrumentally damped dataset. In (f) the black line indicates results from fitting the dataset with percentage change in the lattice parameter and the grey line the shifted dataset.

are also large enhancements in the Clapp configurations *C2*, *C6*, *C15* and *C33*, as well as many of the Clapp configurations containing roughly equal numbers of copper and gold atoms (*C70-87*). These enhancements are what would be expected for a cluster of like atoms. Similar to the effect on the observed Clapp configurations, there is a clear difference between the random and observed Warren-Cowley parameters for the first 10 shells, as can be seen in Figs. 4e and 4f.

Given an awareness of these problems, appropriate steps were taken during data processing to ensure they did not lead to erroneous results in this study.

5. Results and discussion

5.1. Raw data

The raw X-ray diffraction patterns collected during the experiment are shown in Fig. 5. A slight shift in the position of the Bragg peaks with temperature is apparent in these data, corresponding to the lattice parameter change associated with thermal expansion. Likewise, there is the expected increase in the observed Debye-Waller factor.

Three of the data sets (300°C and two at 400°C) show evidence of L1₂ super-lattice peaks. Careful inspection at low 2θ , also identified an apparent increase in the diffuse scattering signal (increased curve to the background at the location of the super-lattice peaks) as the temperature was reduced towards the ordering temperature ($T_c \sim 400^\circ\text{C}$). It should be noted that there are additional small peaks present at $2\theta \approx 3.7^\circ$. These peaks correspond to Cu₂O, that is likely to have formed during the water atomisation process. Fitting the data using a Rietveld refinement, the phase fraction of this impurity was estimated to be $\approx 1.2\%$, which will have no measurable contribution to the PDF.

The change in lattice parameter with temperature is shown in Fig. 6. Overall the variation with temperature is linear. However, there are notable discrepancies in the 300°C and 400°C datasets, and a gradual shift away from the trend in the samples between 410°C and 500°C. This reduction of the lattice parameter on ordering is to be expected, as in the L1₂ structure that forms the Au atoms are surrounded only by Cu atoms, removing the larger Au-Au correlations and allowing the lattice to contract.

5.2. RMC fitting - random box, translations only

RMC fitting was carried out using large box models representing $20 \times 20 \times 20$ supercells of the unit cells obtained from Rietveld refinement (32,000 atoms). The data were corrected for the instrumental resolution, as described previously, using the $S(r)$ function with $\Delta Q = 0.031 \text{ \AA}^{-1}$, calculated from a consideration of the full width at half-maximum of the peaks in the $F(Q)$. RMC refinements were initially carried out using boxes containing a random distribution of atoms, allowing only translational moves and fitting the r -range to the maximum value possible in $\sim 75 \text{ \AA}$ supercells (i.e. $\sim 37.5 \text{ \AA}$). This procedure means that any remaining discrepancies between data and model must be caused by changes

Figure 5: Experimental diffraction patterns as a function of temperature. The data has been truncated in the y -axis, to focus on the changes in the diffuse scattering signal closer to the baseline space. The temperature increases from top to bottom. Datasets labelled in italics were gathered during heating of the as-sprayed sample, those in plain text were obtained during the first cooling ramp and those in bold during the second cooling ramp (see Fig. 1).

Figure 6: Change in lattice parameter of the copper gold alloy with temperature. The black crosses indicate lattice parameters obtained from the Rietveld fits with a random structure and the circles are the lattice parameters obtained from the ordered $L1_2$ structure.

Figure 7: Plot of the difference $T(r)$ s after fitting the data with $20 \times 20 \times 20$ supercells containing a random configuration of atoms using the RMCProfile algorithm, allowing translations only. Datasets labelled in *italics* were gathered during heating from the as-sprayed sample, those in plain text were obtained during the first cooling ramp and those in **bold** during the second cooling ramp (see Fig. 1)

in site occupancy, i.e. chemical ordering in the system. The difference between the experimental PDFs and the calculated values is shown in Fig. 7. From this figure it is immediately obvious that the largest discrepancy is in the 400°C samples. This is unsurprising given that these are two of the three samples that have superlattice Bragg peaks corresponding to the $L1_2$ structure. Comparing these two difference PDFs to that of the 300°C sample it is interesting to note that they appear similar up to around 22-23 Å. As noted in the Bragg data, the 300°C data shows small superlattice peaks that suggest the formation of the $L1_2$ superstructure. This difference PDF suggests that these domains of $L1_2$ are no more than around 2.5 nm in size in the 300°C sample.

In the other datasets, there is little appreciable difference beyond c. 17 Å. The low r region does, however, suggest a systematic change with decreasing temperature. This is apparent in the relative magnitudes of the two peaks in the doublet at 3-4 Å and subsequently in the doublet at 7-8 Å. The development of short-range order into long-range order is likely to proceed in one of two ways. First, a statistical model can be proposed whereby order forms homogeneously throughout the structure, resulting in a change in the observed local concentration in a specific coordination shell compared with the nominal stoichiometry. In this case, order would be limited to only a few correlation shells and exhibited as a difference in the low r -region of the PDF only. Alternatively, micro-domains of an ordered phase can form that gradually grow through the structure. It is likely that such domains would be larger than the typical RMC box size. Consequently, changes will occur across the whole r -range typically used in PDF fitting, with the magnitude of the difference in the PDF increasing with the volume fraction of the material occupied by the domain. The difference PDFs, therefore, suggest that this type of short-range order is better described by a statistical growth model as opposed to a micro-domain growth model.

Figure 8: Plot of the χ^2 values after fitting the data allowing a) only translations and b) then further allowing swaps to occur in the system. Datasets labelled in italics were gathered during heating of the as-sprayed sample, those in plain text were obtained during the first cooling ramp and those in bold during the second cooling ramp (see Fig. 1)

Fig. 8a shows the final χ^2 values from the same fits used to generate the difference PDFs shown in Fig. 7. The differences in these χ^2 values show the quality of the fits under the restriction of randomly distributed atom types in the structure. Therefore, these χ^2 values can be used as indications of the level of chemical short-range order present in the structure at different temperatures, as the quality of the fit should not be temperature dependent if the system has been run for a sufficiently long time to allow convergence. From this graph, the clear additional order present in the structures with identifiable superlattice peaks can be seen by the comparatively large χ^2 value. Above 600°C the fits have the same χ^2 value, suggesting that above this temperature the sample is indeed random. A line has been added to the graph to indicate this ‘random’ baseline, as indicated by the χ^2 . Interestingly, there does appear to be some order present in the low-temperature samples (<300°C). The room temperature sample is the as-sprayed sample and the order present in the sample must therefore be representative of a melt quenched sample of Cu₃Au. This itself is a significant result as it indicates that either some level of ordering must exist in the melt (less likely owing to the lack of order present in the sample close to melting at 900°C), or that the ordering transitions occur fast enough for limited local order to develop during the melt quenching process. As the temperature is increased the comparative level of order reduces, prior to the formation of the superlattice peaks.

Data acquired from the sample at 500°C suggests some level of order exists at this temperature, although possibly different levels of order due to the previous heating regime. The second 500°C measurement was made after the sample was reheated above T_c following the formation of the ordered structure. Therefore, it may be the case that the formation of the additional order at 500°C is due to the fact that the sample was not heated sufficiently to allow the sample to fully randomise. There is also an increase in the level of ordering on cooling between 500°C and 410°C, prior to the appearance of superlattice peaks, suggesting the formation of short-range order in this temperature region, as has been suggested in the literature.

5.3. RMC fitting - translations and swaps

The χ^2 values obtained following RMC fitting, allowing atom types to swap, are given in Fig. 8b. The results show no significant difference in the χ^2 values, which suggests that the system has converged and the additional chemical order has been accounted for. Fig. 9 provides a more detailed comparison of the partial correlation functions obtained from the boxes fitted to the data acquired at 900°C (Fig. 9a) and the 400°C 2nd hour (Fig. 9b), which exhibits the highest level of order. In Fig. 9a there is an apparent difference in the maximum of the partials in the first coordination cell. A closest approach constraint, preventing atoms from forming correlations at shorter distances than a given value, was set in the system at 2.2 Å, but crucially this was the same for all atom types, and no other distance window constraints were applied to the system. As such, this difference in bond length is believed to be real and not a result of the fitting constraints used. This is seen in the data acquired at all temperatures and is

Figure 9: Partial from the output of RMC fits, allowing both translations and atomic swaps, carried out on the data collected at (a) 900°C and (b) 400°C (2nd hour). The red line indicates the Cu-Cu partial, the green line the Cu-Au partial and the blue line the Au-Au partial. Dotted lines indicate the expected peak positions from the lattice parameters. The inset in panel (a) shows how the expected peak positions relate to the lattice parameter in an *fcc* lattice. (Full colour figure should be referenced online)

as would be expected from a hard sphere model considering the relative atomic radii of the Cu (~ 1.28 Å) and Au (~ 1.44 Å) atoms. Moving to higher shells, there is little difference in the maxima of these peaks and instead average values determined by these bond lengths are observed.

Importantly, the difference in atomic size is likely to cause local strain within the lattice. At higher temperatures the lattice is given more vibrational energy and the system is observed to expand. This may offset the disparity in atomic size and relieve some of the strain in the system. At lower temperatures ordering occurs in the system, with the gold atoms becoming surrounded by copper atoms (*C-1* Clapp configuration). This is apparent in Fig. 9b where a reduction in the Au-Au partial is observed. This will result in a concomitant reduction in the lattice strain and a decrease in the lattice parameter, as observed in Fig. 6. Other energetic effects, such as the relative change in bond energies on the formation of more Cu-Au bonds and reduction in Au-Au bonds may also contribute to this ordering effect, but the decrease in local lattice strain is likely to be a strong contributing factor.

5.4. Neutron data

Neutron total scattering data was collected from the room-temperature as-sprayed Cu₃Au powder. For X-ray data the scattering strength is roughly proportional to the atomic number, Z . As such there is a large scattering contrast between Cu ($Z = 29$) and Au ($Z = 79$) atoms. For neutrons, the scattering lengths are $b_{\text{Cu}} = 7.718$ fm and $b_{\text{Au}} = 7.63$ fm [25]. Consequently, the Cu and Au atoms are essentially indistinguishable. It is therefore expected that the level of ordering in a Cu-Au alloy would be essentially invisible in neutron data. As such, neutron scattering provides a method by which it is possible to confirm that the ordering observed in the system from fitting to X-ray data is real, and not merely a consequence of the RMC fitting algorithm.

A comparison of the room temperature fitted datasets using X-ray and neutron radiation are shown in Fig. 10. In the X-ray data there are notable differences in the areas of the partials that make up the later peaks, whilst there are distinct differences in the positions of the peak maxima in the different partials, corresponding to changes in the interatomic distances. In contrast, the partials calculated from the neutron data show no obvious differences. This confirms that the order observed in the box fitted to the X-ray data is likely to be real and not merely an artefact of the fitting algorithm. Similarly, it should be noted that during the 12 hours of fitting the X-ray data the total number of accepted swaps quickly plateaus to a value on the order of 5,000 - 10,000. Fitting the neutron data, however, the atoms were continuously swapped, with a similar number of swaps being performed approximately every 15 minutes, showing that swapping had no effect on the goodness-of-fit.

5.5. Warren-Cowley parameters and Clapp configurations

The output boxes from the RMC runs were analysed using the methods described in previous work [4], calculating the enhancement factors and Warren-Cowley parameters for these systems. The Warren-Cowley α -parameters for the

Figure 10: Partial radial distribution functions from the RMC fits to data acquired from the room temperature as-sprayed sample allowing both translations and swaps for the X-ray and neutron data. The red line indicates the Cu-Cu partial, the green line the Cu-Au partial and the blue line the Au-Au partial. The dotted lines indicate the expected peak positions from the lattice parameters. The insets show the number of swaps as a function of time for the fitting of the two data sets respectively. (Full colour figure should be referenced online)

first ten co-ordination shells, obtained using this method, are shown in Fig. 11a. It can be clearly seen that the 300°C and 400°C data all contain the oscillations that would be expected with L1₂ ordering of the material. At many of the other temperatures it appears that the sample is random. However, there is a distinct change in the first couple of coordination shells. As discussed in the previous work, the Warren-Cowley parameters average some of the finer information in the system and are often less sensitive descriptors of the ordering present in the box. As such, it is perhaps unsurprising that the oscillations dampen faster than might be expected from observation of the difference PDFs. Even so, it is again important to note that there appears to be no systematic increase in all of the coordination shells, but rather an initial increase in the closest coordination shells, providing further indication that the order forming is statistical, as opposed to microdomain. Owing to the inherent random nature of the RMC algorithm, the result of such a refinement is likely to be the least ordered configuration that best represents the data, assuming multiple configurations that yield the same level of fit exist. As such, it will tend to favour configurations representative of statistical ordering. Therefore, conclusions of this nature must be drawn from the difference plots (as already discussed) and confirmed by the means of quantifying the chemical short-range order, and not the other way around.

The Clapp configuration enhancement factors, β , were calculated for a series of boxes run with both translations and swaps fitting the X-ray the PDF data. An example of the enhancement factors calculated from the 900°C data is shown in Fig. 11b. All the enhancement factors are within the bounds of statistical noise, suggesting that the sample is truly random. In comparison, the data obtained from the sample at 400°C (2nd hour), Fig. 11c, shows a distinct pattern of enhancements in specific Clapp configurations. A series of refinements were also run including the Bragg data, which added the additional constraint that the obtained model must agree with the long-range average structure as well as with the short- to mid- range structure described by the PDF. Fig. 12 shows the enhancement factors (for all datasets) for those configurations that are most enhanced and some of the other configurations of interest. For many of the samples, there is a reduction in the *C1* Clapp configuration, panel (b). This indicates that the lattice parameters used in the simulation are correct and the correction for the instrumental resolution has been carried out successfully.

The L1₂ structure is made from only two Clapp configurations: the *C16* and *C-1*. These configurations do show significant enhancement in the data obtained from the sample at 400°C (2nd hour), Fig. 11c. However, several other Clapp configurations also show significant enhancements, which can be rationalised by considering the degradation tree from the Clapp configurations, Fig. 13a. Degradation pathways show how the different Clapp configurations are structurally related, with a variation in local concentration of like and dislike atom types. For a more detailed explanation of these pathways, and an image of the complete degradation tree, see our previous work [4]. Fig. 13a shows the small portion of this tree for the configurations that are observed to be enhanced in this system. The *C16* configuration contains four dislike atoms

Figure 11: (a) Warren-Cowley parameters, α , for the first 10 coordination shells from the fitted boxes for data acquired at all temperature, (b) & (c) Clapp configuration enhancement factors, β , obtained from data acquired at 900°C and 400°C (2nd hour). The dotted lines indicate the bounds of the enhancement factor between which the enhancement can be attributed to statistical variations in the box.

Figure 12: Clapp configuration enhancement factors, β , from the output boxes from the RMCPProfile fits to total scattering data recorded at different temperatures. The dotted lines indicate the upper and lower bounds expected due to statistical variation. The different panels represent specific Clapp configurations a) C-1, b) C1, c) C7 d) C16 e) C17 and f) C34

would be needed to confirm this hypothesis. This also raises questions about the assessment of order in this system in previous *ex situ* studies, where the observed order may be the result of rapid formation during the quenching process.

As the temperature decreased from 500°C to the transition, there was a systematic increase in the *C-1* and *C16* configurations (and related *C7* and *C34*). This can be explained as an increase in the short-range order in the system related to the $L1_2$ structure and is as expected. From the enhancement factors, there is also a notable difference in these configurations between the datasets acquired at 500°C and 600°C, but the difference between the two 500°C datasets is comparatively less than that expected from the χ^2 values.

Some earlier experiments on the Cu_3Au system have suggested that the D0_{22} structure may form during the ordering process to the $L1_2$ structure. Indeed, if the ordering is in response to the strain of the large Au-Au bond distance and occurs entirely to remove this strain by surrounding Au atoms by Cu atoms, then in a Cu_3Au alloy the energetics of the $L1_2$ and D0_{22} structures would be the same. The D0_{22} is formed by the *C-1*, *C16* and *C17* so can be distinguished from the $L1_2$ structure by the presence of the *C17* configuration. This is shown in panel e) of Fig. 12, in which there is an observed increase in the *C17* configuration at all temperatures, apart from after the appearance of the superlattice peaks at 400°C. It should also be noted that, whilst the *C17* configuration increases as the temperature is cooled from 900°C to 600°C, there is little variation in the region 600°C to 410°C. This suggests that the formation of D0_{22} -like order occurs first, as a precursor to the $L1_2$ -type SRO and subsequently disappears on the formation of the $L1_2$ long-range ordered structure. This implies that the ordering that takes place can not be simply a response to a first shell effect, but must have higher shell components.

6. Conclusions

In our previous work a methodology was proposed for the analysis of short-range order in binary alloy systems, using total scattering data. The data presented here, on the Cu_3Au system, have demonstrated the efficacy of this technique for the analysis of subtle variations of order in metallic systems using a combination of pair distribution functions and RMC techniques. By comparing the ordering observed experimentally in the Cu_3Au system with predictions from a theoretical random model allow greater insights to be gained into ordering present, without the need to use one dataset as a systematic baseline for comparison between others. The generation and fitting of simulated datasets highlighted potential artefacts in obtained models that could result from incorrect data processing. Avoiding such errors is of vital importance if a correct determination of the order present in the system is to be successfully accomplished.

Cu_3Au was observed to undergo an ordering transition, to the $L1_2$ structure at $\sim 400^\circ\text{C}$, in agreement with values from literature. This transition was apparent both in the appearance of superlattice peaks in the Bragg data and the change in the area under the peaks in the PDF, as predicted in earlier

theoretical work [4]. Prior to the transition, different levels of short-range order were also apparent, evidenced by changes in the PDFs, demonstrating the high-level of information content available through this methodology. By considering the Clapp configuration enhancement factors and the fitting χ^2 values, a systematic increase in the ordering was identified in the temperature range $400 < T < 500^\circ\text{C}$. The order identified confirms previous reports of the existence of short-range order in the region $400 < T < 600^\circ\text{C}$. By evaluating the Clapp configuration enhancement factors, the increased configurations (*C-1*, *C7*, *C16*, *C34*) clearly identify the type of ordering as being related to the L1_2 formation. The presence of *C17* configurations in the output revealed the presence of some D0_{22} type ordering, which forms as a precursor to the long-range ordered L1_2 structure, and is removed upon long-range ordering.

The identification of order in the melt-quenched sample suggested that local ordering in this system may occur much faster than previously expected. Many of the previous studies on this system have identified order in *ex situ* samples. Given the rate at which order forms in this sample, it is possible that these previously measured levels of order could be the result of ordering during the quenching process, as opposed to the thermodynamically stable state at the quenching temperature. The identification of different levels of order at 500°C , could suggest that the system was not sufficiently randomised prior to the second total scattering measurement; hence the order exhibited in the region prior to the transition could be growth of an ordered region that was nucleated at a lower temperature. Further *in situ* studies are required to identify the true level of order that is thermodynamically stable in this crucial region.

Examination of the partials PDFs calculated from the RMC-obtained models, revealed differences in the relative bond length distributions for the different bond types at all temperatures. This is as expected from the relative sizes of the atomic radii of Cu and Au. These differences were not seen in the model obtained from fitting to neutron total scattering data; the neutron scattering lengths of Cu and Au are similar enough to render them indistinguishable. This further illustrates the impressive level of information available from the PDF. The datasets exhibiting superstructure peaks show a distinct decrease in the occupation of the Au-Au partial in the first coordination shell, resulting in a reduction of the largest interatomic distances and hence a contraction in the observed lattice parameter and a decrease in local lattice strain. Finally a comparison of the difference plots obtained from fitting the data with a random atomistic configuration, suggested that the formation of the order in this structure occurs continuously throughout the system, rather than in the growth and expansion of ordered micro-domains. This was also confirmed by the observed fluctuations in the Warren-Cowley parameters and further supports that this is the mechanism through which order develops in Cu_3Au .

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References

- [1] W. L. Bragg, The diffraction of short electromagnetic waves by a crystal, *Proc. Cambridge Philos. Soc.* 17 (1) (1913) 43–57.
- [2] R. L. McGreevy, L. Pusztai, Reverse Monte-Carlo simulation: A new technique for the determination of disordered structures, *Mol. Simul.* 1 (6) (1988) 359–367.
- [3] H. Y. Playford, L. R. Owen, I. Levin, M. G. Tucker, New insights into complex materials using reverse monte-carlo modeling, *Annu. Rev. Mater. Res.* 44 (2014) 429–449.
- [4] L. R. Owen, H. Y. Playford, H. J. Stone, M. G. Tucker, A new approach to the analysis of short-range order in alloys using total scattering, *Acta Mater.* 115 (2016) 155–166.
- [5] H. Okamoto, D. Chakrabarti, D. Laughlin, T. Massalski, The au-cu (gold-copper) system, *Bulletin of Alloy Phase Diagrams* 8 (5) (1987) 454–474.
- [6] J. M. Cowley, An approximate theory of order in alloys, *Phys. Rev.* 77 (5) (1950) 669–675.
- [7] P. C. Clapp, Atomic configurations in binary alloys, *Phys. Rev. B* 4 (2) (1971) 255–270.
- [8] B. Borie, B. E. Warren, Study of the change in Cu_3Au near 600°C , *J. Appl. Phys.* 27 (1956) 1562.
- [9] C. Walker, D. Keating, A reanalysis of the short-range order in Cu_3Au , *J. Appl. Phys.* 34 (8) (1963) 2309.
- [10] J. M. Cowley, Short-range order and long-range order parameters., *Phys. Rev* 138 (5A) (1965) 1384–1389.
- [11] S. Moss, X-ray measurement of short-range order in Cu_3Au , *J. Appl. Phys.* 35 (12) (1964) 3547.
- [12] S. C. Moss, P. C. Clapp, Correlation functions of disordered binary alloys III, *Phys. Rev* 171 (3) (1968) 764.

- [13] P. Bardhan, J. Cohen, A structural study of the alloy Cu_3Au above its critical temperature, *Acta Crystallogr., Sect. A: Found. Crystallogr.* 32 (1976) 597.
- [14] T. Proffen, V. Petkov, S. Billinge, T. Vogt, Chemical short range order obtained from the atomic pair distribution function, *Z. Kristallogr.* 216 (2) (2001) 47–50.
- [15] T. Proffen, R. Neder, Discus: A program for diffuse scattering and defect-structure simulation, *Journal of Applied Crystallography* 30 (2) (1997) 171–175.
- [16] D. A. Keen, A comparison of various commonly used correlation functions for describing total scattering, *J. Appl. Crystallogr.* 34 (2001) 172–177.
- [17] M. Basham, J. Filik, M. T. Wharmby, P. C. Y. Chang, B. El Kassaby, M. Gerring, J. Aishima, K. Levik, B. C. A. Pulford, I. Sikharulidze, D. Sneddon, M. Webber, S. S. Dhesi, F. Maccherozzi, O. Svensson, S. Brockhauser, G. Náray, A. W. Ashton, *Data Analysis WorkbeNch (DAWN)*, *Journal of Synchrotron Radiation* 22 (3) (2015) 853–858.
- [18] H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *Journal of Applied Crystallography* 2 (2) (1969) 65–71.
- [19] A. C. Larson, R. B. V. Dreele, General structural analysis system (GSAS), Los Alamos National Laboratory Report LAUR (2000) 86–748.
- [20] A. K. Soper, GudrunN and GudrunX : programs for correcting raw neutron and X-ray diffraction data to differential scattering cross section, Rutherford Appleton Laboratory Technical report (2011) RAL–TR–2001–013.
- [21] A. Soper, E. Barney, Extracting the pair distribution function from white-beam x-ray total scattering data, *Journal of Applied Crystallography* 44 (4) (2011) 714–726, cited By 35.
- [22] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin, Q. Hui, RMCProfile: reverse Monte-Carlo for polycrystalline materials, *J. Phys. : Condens. Matter* 19 (33).
- [23] O. Arnold, J. Bilheux, J. Borreguero, A. Buts, S. Campbell, L. Chapon, M. Doucet, N. Draper, R. F. Leal, M. Gigg, V. Lynch, A. Markvardsen, D. Mikkelsen, R. Mikkelsen, R. Miller, K. Palmen, P. Parker, G. Passos, T. Perring, P. Peterson, S. Ren, M. Reuter, A. Savici, J. Taylor, R. Taylor, R. Tolchenov, W. Zhou, J. Zikovsky, Mantid—data analysis and visualization package for neutron scattering and μ SR experiments, *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 764 (2014) 156 – 166.
- [24] G. E. P. Box, M. E. Muller, A note on the generation of random normal deviates, *Ann. Math. Stat.* 29 (1958) 610–611.

- [25] V. F. Sears, Neutron scattering lengths and cross sections, *Neutron News* 3 (3) (1992) 26–37.
- [26] B. Roberts, G. Vineyard, Short range order coexisting with long range order in Cu_3Au , *J. Appl. Phys.* 27 (3) (1956) 203–206.