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[redacted]

# the Ag–Au system

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atom, and (2) a set of interaction energies $\{J_\Gamma\}$ among the various sites belonging to a

expansion techniques [1, 27–30]

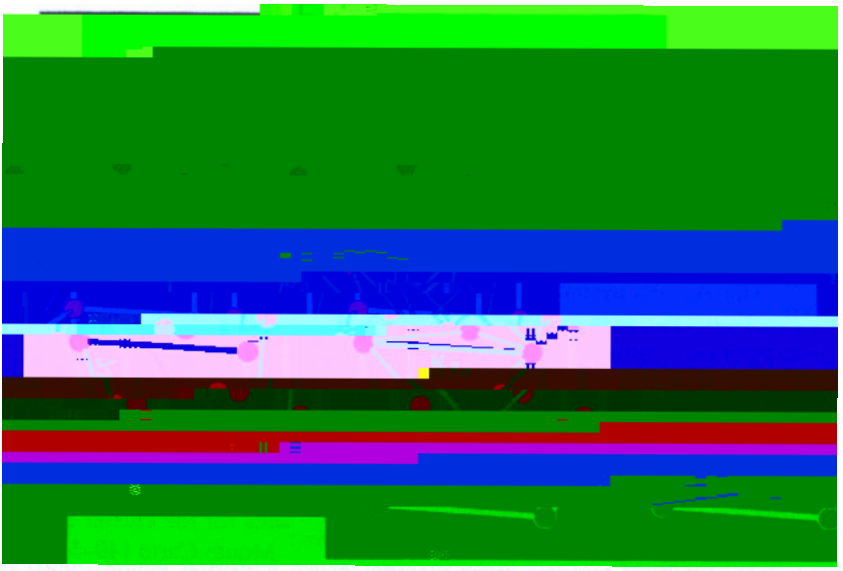


**Figure 1.** Geometric figures used in our cluster expansion. The expansion includes pair figures, three-body figures, and four-body figures. See table 3 for the definition of the figure coordinates.

many-body terms). We determine the $N_J$ interaction parameters $\{J_F\}$ by mapping $N_\sigma$ directly calculated $\Delta E_{\rm direct}(\sigma)$ values onto $\Delta E_{\rm CE}(\sigma)$ of equation (3) through a least-squares fitting procedure, i.e. by minimizing

$$\sum_{\sigma_s}^{N_\sigma} |\Delta E_{\rm direct}(\sigma_s) - \Delta E_{\rm CE}(\sigma_s)|^2 = \min \tag{4}$$

with respect to $J_F$. Convergence is tested by applying equation (3) to a set of structures $\{\sigma_s\}$ not used in constructing the cluster expansion for equation (4). We define the prediction

[illegible] fcc solids [illegible] volume $\Delta V(\sigma)$ for the [illegible] e wave (LAPW) [illegible] Ag and Au using the LDA-based full-potential linearized augmented pla[illegible] method [54, 55]. We have used the LDA exchange–correlation poten[illegible] and 4.0782 Å, respectively. [illegible] [illegible] experimental data [48] of 4.080 Å [illegible] parameters of Ag and Au by 1.9% and 0.05 Å, respectively. Our [illegible] current lattice param[illegible] e difference between the present result and those of Wei et al is due mainly to a different exchange–correlation potential (Wigner form) [59] used in [3]. We have calculated the excess total energies $\Delta E_{\rm direct}(\sigma, V)$ of equation (2) for $N_\sigma = 32$ ordered structures $\{\sigma\}$ [illegible] involving a small number of atoms in the unit cell (up to 8 atoms/cell) [5]. Figure 2 shows

examples of [illegible] simple fcc-based ordered structures [illegible] in our calculations. Table [illegible] and its caption [illegible] these structures. [illegible] of these structures can be describ[illegible] as [illegible] period $A_mB_n$ superlattices along some orientation as shown in figure 2 and [illegible] table 1. The [illegible] calculat[illegible]

[illegible] relaxation lowers the energy of the [illegible] [illegible] are small here (e.g. for Au–Au [illegible] structure by [illegible] 15 meV/atom). To obtain [illegible] Au system, relaxation lowers the energy of the $L1_0$ [illegible] g scheme that is geometrically [illegible] infinitely precise results we use a k-point sampling [illegible]

**Table 1.** The directly calculated LAPW excess energies $\Delta E_{\text{direct}}(\sigma)$ (error $\sim \pm 2$ meV/atom) (equation (2)), the cluster-expanded energy $\Delta E_{\text{CE}}(\sigma)$ (equation (3)), and the prediction error

**Table 2.** This table illustrates the effects of $k$-point sampling on the calculated $\Delta E_{\text{direct}}$ (in meV/atom) of some ordered compounds. The structures are defined in table 1. We have used the equivalent $k$-point sampling scheme of [60]; these two $k$-point sets are equivalent to 60 and 408 fcc special $k$-points, respectively (see [58]). We also give the actual number of $k$-points, $N_k$, in the irreducible zone for a particular structure.

| | | 60 equiv. fcc $k$-points | | 408 equiv. fcc $k$-points | |
|---|---|---|---|---|---|
| Structure | Formula | $N_k$ | $\Delta E$ | $N_k$ | $\Delta E$ |

(AB). Using this original Connolly–Williams procedure, we obtained an average prediction error of $\delta_{PE} = 1.6$ meV/atom and a maximum prediction error of 4.4 meV/atom for 27 other structures that are not used in obtaining the interaction $J$ values. The prediction errors for some specific structures are unsatisfactory. For example $\delta_{PE}$ are 4.4, 2.4, 3.0, 2.6 meV/atom, for structures '40', $\gamma 2$, $DO_{22}$ ($AgAu_3$), and W3, respectively (larger than the estimated error of direct LDA calculation of 2 meV/atom). The large error for '40' and $DO_{22}$ is because the Connolly–Williams set of interactions creates a spurious degeneracy

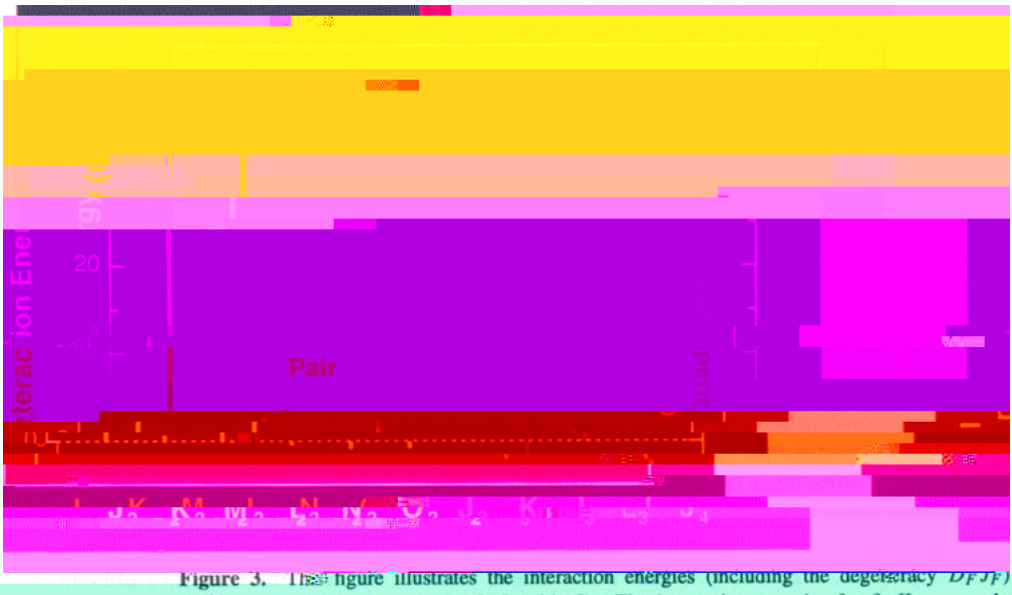



**Figure 3.** The figure illustrates the interaction energies (including the degeneracy $D_F J_F$) used in this work (figure 1) for fit I (table 3). The interaction energies for fit II are nearly indistinguishable on this scale. Note that the nearest-neighbor pair interaction $J_2$ is dominant.

Here $\mathcal{J}$ denotes the definition of the 'figures' $F$ used in our cluster expansion in terms of the

Cluster type Designation in figure Value

Triplets $J_3$ (000) (110) (101)

−0.56 −0.06

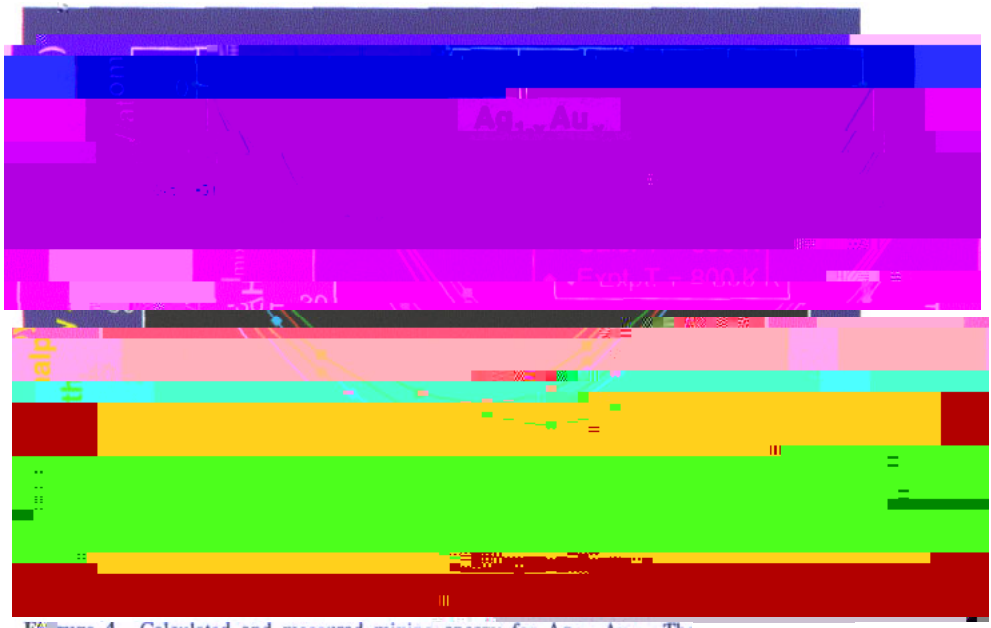


**Figure 4.** Calculated and measured mixing energy for $Ag_{1-x}Au_x$. The $T = 800$ K, lozenges) are cited from [23]. We give the calculated values

**Table 4.** The experimental [23] and calculated (fit I) $Ag_{1-x}Au_x$ mixing enthalpy $\Delta H_{mix}$ (meV/atom) using (i) Monte Carlo simulation at $T = 800$ K (including the short-range order effects and (ii) equation (6) corresponding to the completely ran

| | $\Delta H(x, T = 800\ \mathrm{K})$ | | $\Delta H(x, T \to \infty)$ | |
|---|---|---|---|---|
| | Exptl. | Monte Carlo | Calc. (equation (6)) | |
| $x$ | $T = 873$ K | $T = 800$ K | $T = \infty$ | |
| 0.0 | 0.0 | 0.0 | 0.3 | 0.3 |

**Table 5.** The order–disorder phase transition temperatures $T_c$ for $Ag_{1-x}Au_x$ alloys at $x = \frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. The calculated results were obtained using $N_J$ interactions, solving the ensuing Ising model with the Monte Carlo (MC) method or with the cluster variation method (CVM). The 'measured' data were obtained by (i) using an inverse Monte Carlo method to extract three composition-dependent effective pair interactions from the short-range order data of the Georgopoulos–Cohen (GC) and Borier–Sparks (BS) analyses and (ii) subjecting the these effective interactions to a direct Monte Carlo simulation.

| | | $Ag_3Au$ $L1_2$ | AgAu $L1_0$ | $AgAu_3$ $L1_2$ |
|---|---|---|---|---|
| Calculated (K) | | | | |
| *Present, fit I* | $N_J = 12$; MC | 155 | 210 | 225 |
| Wei *et al*[a] | $N_J = 5$; CVM | 120 | 240 | 200 |
| Mohri *et al*[b] | $N_J = 5$; CVM | 152 | 177 | 183 |
| 'Measured' (K) | | | | |
| Schönfeld *et al* (BS)[c] | $N_J = 3$; MC | 115 | 115 | 155 |
| Schönfeld *et al* (GC)[d] | $N_J = 3$; MC | 165 | 165 | 210 |
| Norman and Warren[e] | | 90 | | |
| Ziesemer[f] | | | 168 | |

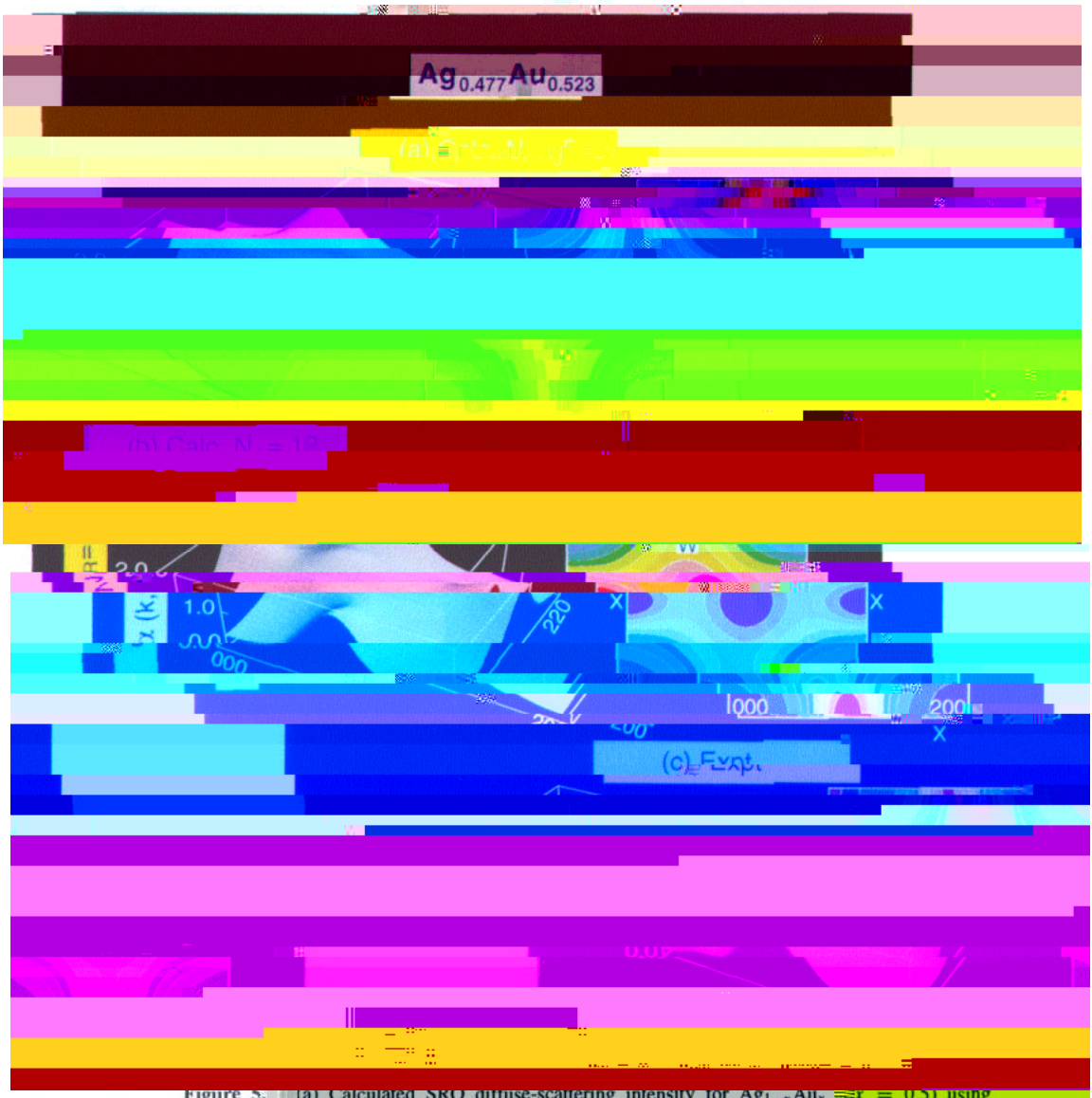



Figure 5. (a) Calculated SRO diffuse-scattering intensity for $Ag_{1-x}Au_x$ ($x = 0.51$) using Connolly–Williams set of nearest-neighbor $N_J = 5$ interaction energies, (b) calculated SRO map using our set of $N_J = 12$ interaction energies, and (c) experimental diffuse-scattering intensity due to short-range order $\alpha(\mathbf{a}, r_R)$ for $Ag_{0.477}Au_{0.523}$, which were Fourier-synthesized using $N_R = 13$ real-space $\alpha(r_R)$.

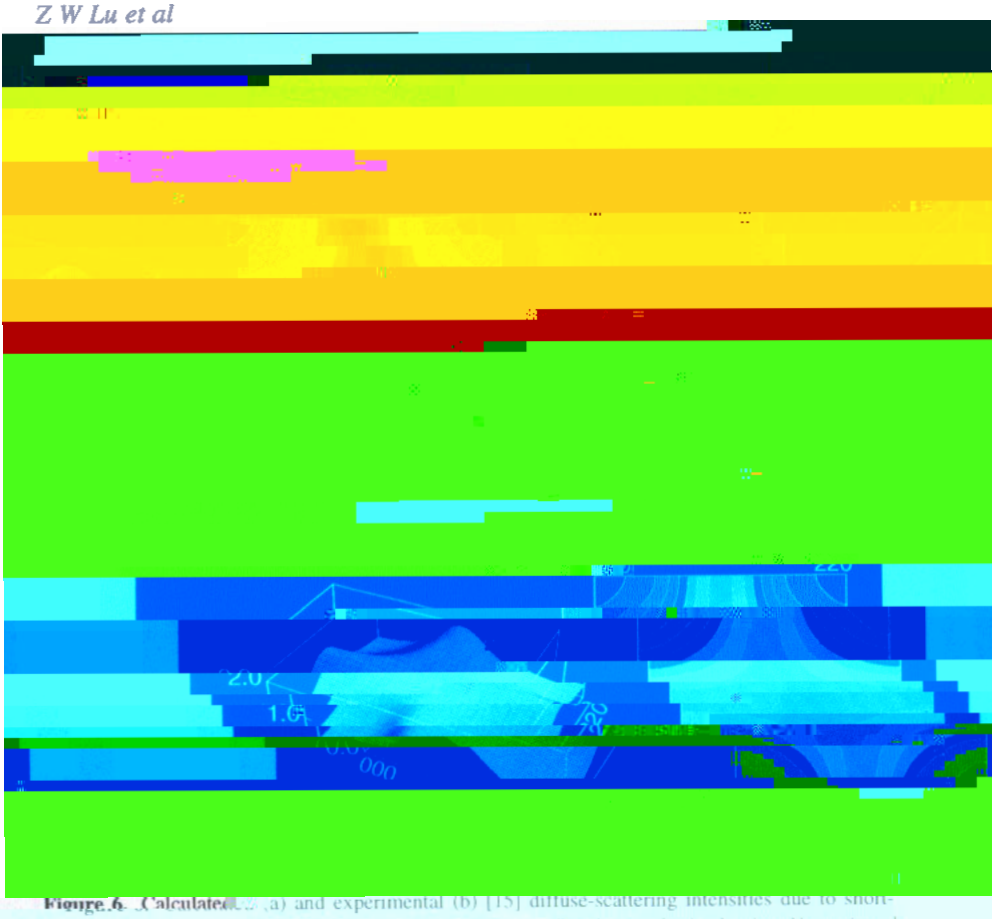



**Figure 6.** Calculated (a) and experimental (b) [15] diffuse-scattering intensities due to short-range order in Cu$_{85}$Au$_{15}$ alloys, obtained by Fourier synthesizing $\alpha(\kappa_{lmn})$ in reciprocal space $\alpha(\kappa_{lmn})$ (including $\alpha(\kappa_{000}) \equiv 1$ for both experiment and theory). The calculation was done at $T = 600$ K, while the experiment was performed on a sample that was homogenized at $T = 1173$ K and later aged at $T = 515$ K.

mixing

values with experiment [23]. The agreement is excellent. Note that the finite-temperature

enthalpy

and by Ackland and Vitek [25] and the semiempirical method by Bozzolo and coworkers

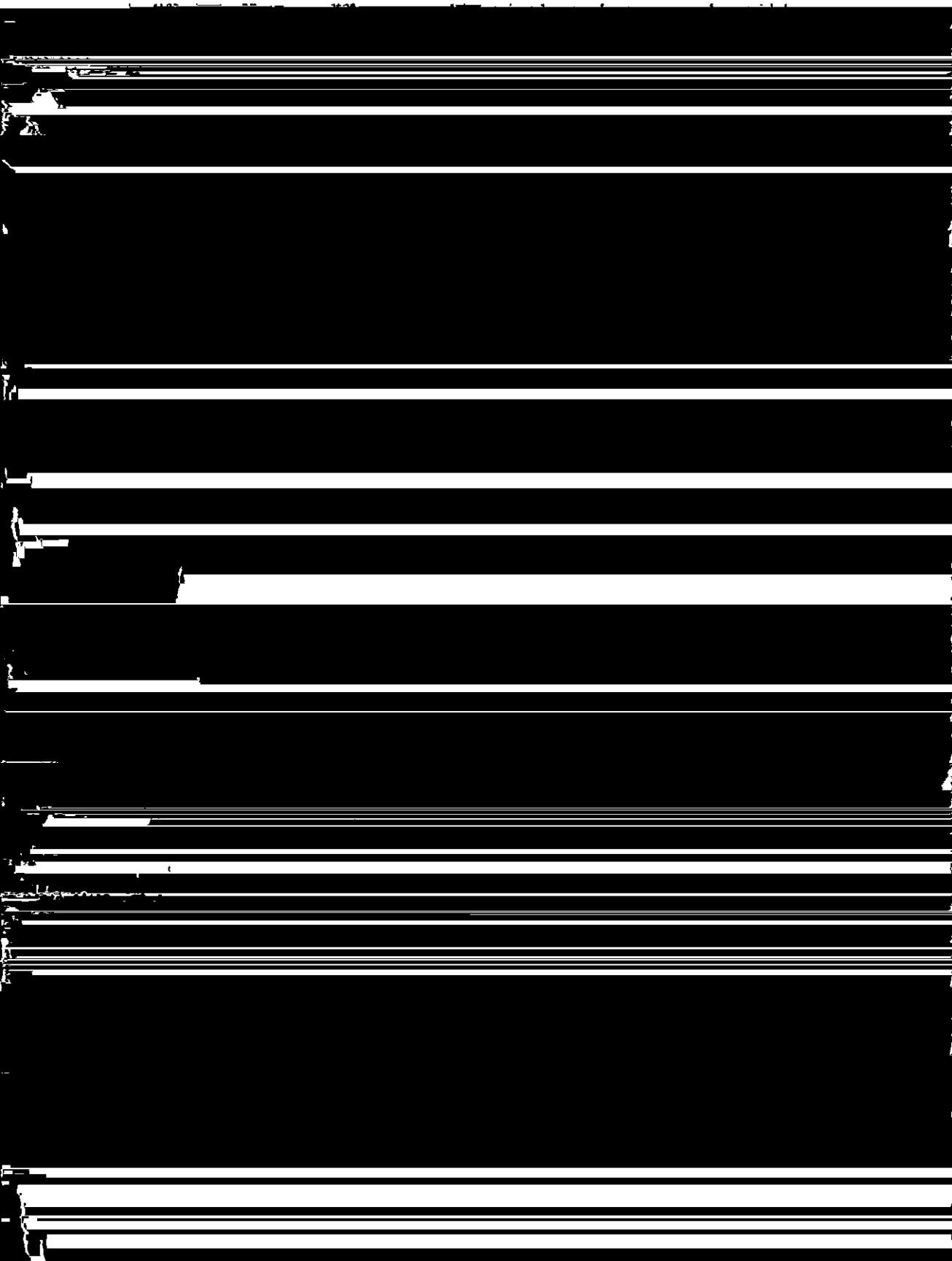
order map correctly reproduce the shape and composition dependence of the short-range

### 3.4. $T = 0$ ground state structures

The ground state problem can be solved using the linear programming method [61, 62]. For

short-ranged alloy systems, the most complete searches for the ground state were given by Kan


**Figure 7.** Calculated (a) and experimental (b) [15] diffuse-scattering intensities due to short-range order $\alpha(k, N_R)$ for $Ag_{0.750}Au_{0.750}$, which were Fourier synthesized using $N_R = 210$ real-space pairs in $(K)_{mn}$ (including $\alpha(R_{000}) = 1$ for both experiment and theory). The calculation was done at $T = 600$ K.



difference at $x = 0.5$ is $-4.4$ meV/atom, correlating with a fairly pronounced peak at the $X$ point for $\alpha_{\mathrm{SRO}}(k)$ at $x = 0.523$.

## 4. Conclusions

We have demonstrated here that accurate alloy properties can be obtained from *ab initio*

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