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Monte Carlo simulations in Au₃Cu

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Résumé. — L'énergie des alliages Au-Cu riches en Au est décrite par le modèle d'Ising. Les 4 premiers potentiels d'interaction sont calculés à partir des expériences de diffusion diffuse faites sur Au₇₅Cu₂₅ et Au₇₀Cu₃₀. Ces potentiels sont comparés aux résultats obtenus par d'autres méthodes (formule de Clapp et Moss, CVM inverse). A partir des potentiels calculés, on montre que l'on peut expliquer les expériences de calorimétrie différentielle et que l'énergie des fluctuations est une partie importante des enthalpies de transformation ordre-désordre mesurées.

Abstract. — The energy of the Au-rich AuCu alloys is written in the Ising Model. The first 4 interaction potentials are calculated from the diffuse scattering experiments in Au₇₅Cu₂₅ and Au₇₀Cu₃₀. These potentials are compared to the results of other methods (Clapp-Moss formula, Inverse CVM method). It is shown that the calculated potentials can quantitatively account for the D.S.C. experiments, and that the energy of the fluctuations are an important part of the transition enthalpies deduced from the experiment.

Introduction.

The short-range order parameters above the order-disorder transition in Au₃Cu have been precisely measured [1, 2]. From these measurements, one can deduce the interactions involved in the transition. Here, an Ising Model with 4 nearest neighbour interactions is used. The energy of the system is written [3] \( H = 2 \sum_i V_i N_{AA}(i) \) where \( N_{AA}(i) \) is the number of Cu atom pairs at distance \( i \) and \( i \) indicates the index of the shell of neighbours involved (here : 110, 200, 211 and 220 in the usual 2 h, 2 k, 2 l cubic indices). In this model, the lattice is rigid and the elastic interactions are neglected. From the results obtained, the thermodynamical properties of this system can be explained : transition temperatures, nature of the low temperature phase, temperature evolution of the energy of order in the system.

In the case of Au₃Cu, the interaction energies have been calculated by the Clapp and Moss formula and by the inverse CVM approximation [2, 4]. Here, the interaction energies are calculated by the Inverse linearized Monte Carlo Method [5].

1. The Inverse Linearized Monte Carlo method applied to Au₃Cu.

The first 4 interaction energies are deduced from the following equations:

\[
\alpha_i^{\text{calc}}(V_1, V_2, V_3, V_4, T) = \alpha_i^{\text{meas}}(T). \tag{1}
\]

Where the \( \alpha_i \) are the usual Warren Cowley short range order parameters and \( i \) is the index of the neighbouring shell.

The measured \( \alpha_i^{\text{meas}} \) are deduced from the analysis of the diffuse scattering experiments and the calculated \( \alpha_i^{\text{calc}} \) are obtained from the Monte Carlo method using the Metropolis [6] algorithm with a system of 4,000 atoms. These equations are linearized via an approximate calculation of the first order partial derivatives (a complete derivation is given in [5]). Here, only the results obtained at 573 K \( (T/T_c \approx 1.2, T_c \text{ is the order-disorder transition temperature}) [1, 2] \) with single crystals of Au₀.₇₅Cu₀.₃₅ and Au₀.₇₀Cu₀.₃₀ are used. In practice, the calculations are carried in two steps.
1.1 4 EQUATIONS WITH 4 UNKNOWN VARIABLES. — A solution can be deduced from the simple linearization of the first 4 equations (1) by an iterative process [5] (Newton-Raphson method). In this case, since the temperature of measurement $T$ is not close to the transition temperature $(T/T_c = 1.2)$, the nonlinearities are small and convergence is easy. Table I shows the results obtained. The agreement between the calculated and the measured short range order parameters is excellent. The interaction energies given here are twice the interaction energies used by Bessière et al. [1, 2]). Errors in $V_i$ are deduced from the experimental errors given in [2].

1.2 28 EQUATIONS. — Here, the method holds in a least square fit and is limited to 28 equations by our choice of the M.C. lattice. One has to minimize $r^2$ in:

$$r^2 = \sum_{i=1}^{28} \left[ \frac{\alpha_i^\text{calc}(V, T) - \alpha_i^\text{meas}(T)}{\sigma_i^\text{meas}} \right]^2 \quad (2)$$

where $\alpha_i^\text{meas}$ is the experimental mean square root deviation on $\alpha_i^\text{meas}(T)$. In a linearized approximation, close to the minimum of $r^2$, it is assumed that one can write:

$$r^2(V_0 + \delta V) = x^2 + \delta V^T C \delta V. \quad (3)$$

In the 4-dimensional space $V$, $\delta V = V - V_0$, $V_0$ is the solution corresponding to the minimum and (neglecting higher order derivatives) the matrix elements of $C$ can be written:

$$C_{ik} = \sum_{i=1}^{28} \frac{\partial \alpha_i^\text{calc}}{\partial V_i} \frac{\partial \alpha_i^\text{calc}}{\partial V_k} / |\sigma_i^\text{meas}|^2. \quad (4)$$

Starting from the solutions of the first method (Tab. I), the minimum of $r^2$ can be found by iterations (See [5]). In the case of Au$_7$Cu, the minimum value of $r^2$ is obtained close to the initial values of the interaction energies. Nevertheless, this minimum ($x^2$) is somewhat higher than the value expected in a "chi-squared test" used in statistical analysis if the $\alpha_i^\text{meas}$ are independent parameters [7] (in such a case $x^2 = 24 \pm 7$): the result is 128 in Au$_{75}$Cu$_{25}$ and 36 in Au$_{70}$Cu$_{30}$. This indicates that either the model used (4 potentials) is not satisfactory or the errors in [2] are underestimated. A careful comparison of $\alpha_i^\text{meas}$ with $\alpha_i^\text{calc}$ carried in Au$_{75}$Cu$_{25}$ seems to indicate that only small but fairly extended $V(r)$ can lower the discrepancy. This discrepancy remains small.

Figure 1 shows the diffuse scattering (in Laue units) obtained by the Fourier Transform of the first 28 $\alpha_i$ (and $\alpha_0 = 1$) in the case of Au$_{0.75}$Cu$_{0.25}$. The curve calculated from the $V_i$ of table I is close to the curve obtained from the measured $\alpha_i$. As many corrections are carried in [1, 2] (background, calibration, separation of size effects...), the resulting $\alpha_i^\text{meas}$ may not be completely independent parameters and the (small) errors given in [2] may be somewhat underestimated.

It is now assumed that the experimental errors in

<table>
<thead>
<tr>
<th>Site</th>
<th>$V_i^\text{mev}$</th>
<th>$\alpha_i^\text{calc}$</th>
<th>$\alpha_i^\text{meas}$</th>
<th>$V_i$ (meV)</th>
<th>$\alpha_i^\text{calc}$</th>
<th>$\alpha_i^\text{meas}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>10.54(1.03)</td>
<td>-0.0719(5)</td>
<td>-0.0710(30)</td>
<td>10.14(1.4)</td>
<td>-0.0743(4)</td>
<td>-0.0740(50)</td>
</tr>
<tr>
<td>200</td>
<td>-6.62(0.94)</td>
<td>0.1060(13)</td>
<td>0.1030(50)</td>
<td>-5.51(1.1)</td>
<td>0.1067(9)</td>
<td>0.1068(60)</td>
</tr>
<tr>
<td>211</td>
<td>2.76(0.64)</td>
<td>-0.0273(5)</td>
<td>-0.0270(30)</td>
<td>3.25(0.7)</td>
<td>-0.0324(4)</td>
<td>-0.0330(30)</td>
</tr>
<tr>
<td>220</td>
<td>-0.66(0.60)</td>
<td>0.0448(11)</td>
<td>+0.0440(30)</td>
<td>-0.43(0.7)</td>
<td>0.0473(7)</td>
<td>0.0480(40)</td>
</tr>
</tbody>
</table>

Table I. — Interaction energies (in meV) deduced from the first 4 short-range order parameters.
Au_{75}Cu_{25} and in Au_{70}Cu_{30} have to be multiplied by 2.2 and 1.2 respectively in order to obtain a good value of $\chi^2$. In fact, the results of successive iterations from formula (3) are not very stable. In each step, $C^{-1}$ must be calculated. As the $C_{ik}$ in (4) are calculated by small variations of $V_i$ and $V_k$, the results have a poor precision

$$\left(\sigma(C_{ik})/|C_{ik}| \sim 0.05\right).$$

On the other hand, $C$ is ill conditioned, as can be seen from its diagonalization (Tab. II). The precision in calculating $C^{-1}$ is hazardous. In our approximation, all the eigenvalues ($\lambda_j$) of $C$ must be positive. The smaller eigenvalues (Tab. II) can then indicate an instability of the minimum of $\chi^2$ in the 4-dimensional $V$ space along the corresponding eigenvector.

For these reasons, a second calculation of (3) and (4) is carried in the $V$ space using a new base calculated from the eigenvectors ($u_i$) of $C$ in Au_{70}Cu_{30}. In this new base, the smaller eigenvalues can be precisely calculated by a strong increase of $V_i$ in the direction of the corresponding eigenvector. Table III shows the results obtained. The eigenvalues are obtained with a reasonable accuracy and it is clear that $\chi^2(V_0)$ is at a minimum. From these eigenvalues an estimate of the volume of errors can be given. This is a 4-dimensional ellipsoid, the principal directions of which are close to the eigenvectors $u_i$.

The length of the corresponding axis is $\lambda_j^{-1/2}$. From these values, a mean square root deviation (called errors) in determining the $V_j$ separately can be obtained (the best estimates of $\lambda_j$ are given in Tab. III).

### 1.3 COMPARISON OF THE RESULTS

Table IV summarizes the results obtained from the two methods here discussed, the Clapp and Moss (CM) formula (called Random Phase Approximation in [2]) and the Inverse CVM method [2] explained in [4] with the quadruple tetrahedron-octaedron for maximum cluster.

As usual, $V_1$ is higher in the M.C. method than in the Clapp and Moss formula. This is due to the « frustration » of the antiferromagnetic first neighbour interactions in FCC systems. It is the impossibility to alternate A and B atoms when odd rings of nearest neighbour atoms are present in the structure [8]. The other interaction energies obtained from these two methods are close together.

On the contrary, strong discrepancies are observed between our results and the Inverse CVM method in the estimation of $V_3$ (see Tab. IV).

From the two sets of 28 $\alpha$ measured at 573 K on Au_{75}Cu_{25} and Au_{70}Cu_{30}, two 4-dimensional error ellipsoids are calculated. It has been verified that the two ellipsoids overlap. This means that the interac-

### Table II.

<table>
<thead>
<tr>
<th>$V_i$ (meV)</th>
<th>Matrix C (symmetric, meV$^{-2}$)</th>
<th>$\lambda_j$</th>
<th>Eigen vectors $u_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{75}$Cu$</em>{25}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.54</td>
<td>1.64 - 2.95 2.65 - 4.50</td>
<td>39.12</td>
<td>-0.15736 0.40883 -0.47856 0.76097</td>
</tr>
<tr>
<td>-6.62</td>
<td>7.59 - 7.11 18.87</td>
<td>2.12</td>
<td>-0.28244 0.47883 0.80856 0.19283</td>
</tr>
<tr>
<td>2.77</td>
<td>10.56 - 13.64 23.24</td>
<td>1.33</td>
<td>-0.4004 0.58826 -0.34184 -0.61382</td>
</tr>
<tr>
<td>-0.66</td>
<td></td>
<td>0.39</td>
<td>0.85741 0.507 0.01888 -0.08346</td>
</tr>
</tbody>
</table>

| Au$_{70}$Cu$_{30}$ |                                |            |                      |
| 10.03        | 4.99 - 8.36 8.27 - 16.53        | 119.6      | -0.17318 0.36851 -0.50347 0.76206 |
| -6.15        | 17.58 - 20.75 33.70             | 8.09       | -0.35519 0.2201 0.83768 0.37082 |
| 3.35         | 36.01 - 43.27 70.91             | 1.34       | -0.28700 0.80098 -0.09669 -0.51644 |
| -0.21        |                                | 0.51       | 0.88050 0.41735 0.18834 0.12271 |
Table IV. — Potentials in Au$_3$Cu calculated from various methods (errors in parentheses).

<table>
<thead>
<tr>
<th></th>
<th>4 $\alpha_i$ (meV)</th>
<th>28 $\alpha_i$ (meV)</th>
<th>(RPA) Clapp-Moss</th>
<th>C.V.M. Inverse</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{75}$Cu$</em>{25}$</td>
<td>10.54(1.03)</td>
<td>10.15(2.0)</td>
<td>9.88</td>
<td>12.74</td>
</tr>
<tr>
<td></td>
<td>- 6.62(0.94)</td>
<td>- 7.5 (1.5)</td>
<td>- 5.26</td>
<td>- 7.46</td>
</tr>
<tr>
<td></td>
<td>2.76(0.64)</td>
<td>1.9 (0.8)</td>
<td>2.44</td>
<td>8.22</td>
</tr>
<tr>
<td></td>
<td>- 0.66(0.6)</td>
<td>- 0.5 (0.9)</td>
<td>- 0.74</td>
<td>- 1.74</td>
</tr>
<tr>
<td>Au$<em>{70}$Cu$</em>{30}$</td>
<td>10.14(1.4)</td>
<td>9.46(1.6)</td>
<td>8.08</td>
<td>12.54</td>
</tr>
<tr>
<td></td>
<td>- 5.51(1.1)</td>
<td>- 6.7 (1.1)</td>
<td>- 4.82</td>
<td>- 6.66</td>
</tr>
<tr>
<td></td>
<td>3.25(0.7)</td>
<td>3.17(0.6)</td>
<td>2.62</td>
<td>+ 8.98</td>
</tr>
<tr>
<td></td>
<td>- 0.43(0.7)</td>
<td>- 0.54(0.6)</td>
<td>- 0.34</td>
<td>- 1.32</td>
</tr>
</tbody>
</table>

Electron energy has no significant change within this composition range.

1.4 INTERPRETATION OF THE MATRIX $C$. — From the calculated eigenvalues, the errors are very small along $\alpha_1$ (Tab. III) and the 4-dimensional ellipsoids of error are very flat in the hyperplane described by:

$$0.17 \delta V_1 - 0.37 \delta V_2 + 0.5 \delta V_3 -$$
$$- 0.768 \delta V_4 = 0.$$

(5a)

For comparison, the same relation has been deduced from the calculation in Ni$_3$Fe [4]

$$0.14 \delta V_1 - 0.36 \delta V_2 + 0.54 \delta V_3 -$$
$$- 0.74 \delta V_4 = 0.$$

(5b)

In the mean-field approximation the transition temperature towards an $L_{12}$ phase is deduced from CM. The plane $kT_c = ct$ can then be written:

$$kT_c = 2 c (1 - c) (4 V_1 - 6 V_2 + 8 v_3 - 12 V_4) = ct.$$

In this case, one obtains:

$$0.248 \delta V_1 - 0.372 \delta V_2 + 0.496 \delta V_3 -$$
$$- 0.744 \delta V_4 = 0.$$

(5c)

These formulae correspond, in the approximations involved, to the hyper plane $kT_c(V) = ct$, close to the solution of (3). The discrepancy observed in the $\delta V_1$ term between (5c) and the two other formulae (5) is attributed to the « frustration ».

In the low temperature $L_{12}$ phase of this system, the antiphase energy $\sigma_a$ is proportional to $- V_2 + 4 V_3 - 4 V_4$. This means that the (0, 1, - 4, 4) vector ($w$) in the $V$ space corresponds to the direction of strong change of $\sigma_a$. It can be shown that ($u_1$, $u_2$, $w$) are almost coplanar, if account is taken of the errors in the determination of these eigenvectors. For this reason, $u_2$ is the direction of the $V$ space of strong change of $\sigma_a$ if $T_c$ is held constant. The second eigenvalue in table III indicates the precision obtained in determining $\sigma_a$, i.e. the stability of the $L_{12}$ simple cubic structure against the $D0_{22}$ tetragonal structure (lattice notation : Strukturbericht [9]).

2. Energy calculations.

The variation of the energy of the system with temperature can be calculated from the M.C. method in the Ising Model. The interactions used (see top of Tab. II) are:

$$V_1 = 10.54, \quad V_2 = - 6.62, \quad V_3 = 2.76$$

and

$$V_4 = - 0.66 \quad \text{(in meV)}.$$

The calculations have been carried out at the two concentrations of the experiment with 6912 FCC lattice sites. Figures 2 and 3 show the results obtained (in J/mole). At low temperatures the $L_{12}$ ordered phase is observed, and $T_c$ can be estimated to be 468 K in Au$_{0.75}$Cu$_{0.25}$ and 493 K in Au$_{0.70}$Cu$_{0.30}$. These results are close to the thermal transition temperatures determined from X-ray measurements by Battermann [10]: 472 K, and 494 K respectively.

Neglecting volume changes, these results can be compared with Differential Scanning Calorimetry (DSC) measurements [1, 11]. In this case, it can be assumed that the enthalpy variation of the system has been measured from an equilibrium value $T_1$ to about 573 K. Since the samples have been aged for a sufficiently long time (1 week) under the transition temperature, they are probably in equilibrium.

Table V compares the results of this calculation with those of the DSC measurements [1]. The agreement is satisfactory. In this system (Figs. 2 and 3), the latent heat of order appears as a small contribution to the DSC measurements. In fact, the increase of the fluctuations close to the transition...
Fig. 2. — Energy of Au$_{75}$Cu$_{25}$ versus temperature calculated from the $V_i$ given in text.

Fig. 3. — Energy of Au$_{70}$Cu$_{30}$ versus temperature calculated from the $V_i$ given in text.

Table V. — Calculated and Measured Enthalpy variations (in J mole$^{-1}$) from $T_i$ to 573 K.

<table>
<thead>
<tr>
<th>Conc</th>
<th>$T_i$</th>
<th>$\Delta H_{\text{meas}}$</th>
<th>$\Delta H_{\text{calc}}$ (from M.C.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{0.70}$Cu$</em>{0.30}$ (disordered)</td>
<td>493</td>
<td>145</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>479</td>
<td>683</td>
<td>665</td>
</tr>
<tr>
<td></td>
<td>448</td>
<td>834</td>
<td>934</td>
</tr>
<tr>
<td>Au$<em>{0.75}$Cu$</em>{0.25}$ (disordered)</td>
<td>479</td>
<td>110</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>453</td>
<td>520</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>1 061</td>
<td>1 030</td>
</tr>
</tbody>
</table>

Discussion.

This calculation of the phase diagram is fairly imprecise. In a narrow temperature range close to the transition, two coexisting phases should appear. This is not observed and this is partly explained by the small size of the M.C. lattice. Nevertheless, no significant change of the energies plotted in figures 2 and 3 have been observed with 2 048 and 4 000 atomic sites under $T_c$-10 K. A better calculation should increase $T_c$ and the two-phase-region should appear close to the $T_c$ calculated here.

In Au$_3$Cu, periodic antiphases (AuCuII) have been observed [1]. These antiphases are very difficult to obtain from the M.C. method (the lattice is small). Moreover, as the antiphase energies calculated here are high, the four calculated $V_i$ cannot explain the Au$_3$CuII phase. This phase appears in a narrow temperature range close to $T_c$. This should have only small effect on the energies in figures 2 and 3.

In this system, the short-range order has been measured closer to $T_c$ [2]. The method described here cannot explain the results obtained at the latter temperatures, where the local order is more developed. This can be explained by the limits of the model used here near $T_c$.

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References