Estimation of the Critical Temperatures of Order-Disorder Phase Transitions in Cu-Au Alloys Using Short-Range Order Parameters

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Abstract. An expression for calculating the critical temperature of order-disorder transition in face-centered cubic alloys is developed with accounting of pairwise interatomic potential in the first eleven shells. The expression obtained was applied to estimate the critical temperatures for Cu_3Au, $CuAu$, and $CuAu_3$ alloys in comparison with experimental data from a phase diagram of the Cu-Au system. Magnitudes of the pairwise interatomic potential in the alloys studied were computed using values of the short-range order parameters which were experimentally obtained from X-ray diffuse scattering intensity. In this computation, the Krivoglaz-Clapp-Moss approximation and Cowley equations were applied.

Introduction

A short-range order in Cu-Au solid solutions has been repeatedly investigated, both experimentally and theoretically [1-13]. According to the phase diagram [14], the Cu-Au system is characterized by complete solutions of two components at high temperatures and with various ordered phases that appears at lower temperatures. The major ordered phases occur at stoichiometric compositions Cu_3Au, $CuAu$, and $CuAu_3$ with critical temperatures T_c of 663 K, 683 K and ~470 K respectively. Both Cu_3Au and $CuAu_3$ in ordered phase have the $L1_2$ superstructure while the low temperature phase of $CuAu$ has the $L1_0$ superstructure. All these superstructures exhibit short-range order above T_c and its short-range order parameters are defined experimentally from X-ray diffuse scattering intensity [1-7,12,13].

Theoretically, the relation between short-range order parameters and pairwise interatomic potentials are useful for description of ordering processes in solid solutions. In the framework of the statistical theory of short-range order, J.M. Cowley derived equations relating short-range order parameters with pairwise interatomic potentials using the method of self-consistent field [15]:

$$2 \sum_j \alpha_j V_{ij} - k_B T \ln\left\{1 + \frac{\alpha_i}{c_A c_B (1-\alpha_i)^2}\right\} = 0, \tag{1}$$

where α_i is the Warren-Cowley short-range order parameter at the i-th lattice site with respect to the central atom, α_j is the short-range order parameter at the j-th site counted from i-th site, c_A and c_B are atomic concentrations of the alloy components, $V_{ij} = \left(V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}\right)/2$ is the pairwise interatomic potential ($i \neq j$, V_{ij}^{AA} corresponds to the interaction between A atoms at sites i and j, etc.), k_B is the Boltzmann constant, and T is absolute temperature. For the Cu_3Au alloy, Eq. 1 was used by J.M. Cowley to calculate values of pairwise interatomic potential on the first three shells via values of short-range order parameters on first ten shells determined experimentally in his work [1]. Also he derived an expression for calculating the critical temperature of order-disorder transition in Cu_3Au and $CuAu$ alloys accounting the pairwise interatomic potential on the first two shells and long-range order parameter.

P.C. Clapp and S.C. Moss [16] derived equations, which relates the scattering intensity $\alpha(\mathbf{k})$ of X-ray produced by short-range order to the Fourier transform of the pairwise interaction potential $V(\mathbf{k})$ in an alloy above its ordering critical temperature T_c. It is written as:

$$\alpha(\mathbf{k}) = \frac{C}{[1+2c_A c_B (1/k_B T)V(\mathbf{k})]}, \tag{2}$$

where C is normalization constant whose value is determined by the condition that integral of $\alpha(\mathbf{k})$ over unit cell of reciprocal lattice be unity. Initially, the Eq. 2 with different values of C was derived in different way by M.A. Krivoglaz [17]. Thus, Eq. 2 was named as the Krivoglaz-Clapp-Moss approximation.

Via Eq. 2, the absolute minima in $V(\mathbf{k})$ must occurs at the reciprocal lattice points where $\alpha(\mathbf{k})$ is a maximum in the ordered phase. The critical point can thus be defined as the temperature for which the denominator in Eq. 2 goes to zero at the appropriate place in reciprocal space. Therefore the equation for defining the critical temperature T_c is:

$$1 = -2c_A c_B (1/k_B T_c)V(\mathbf{k}_m), \tag{3}$$

where $V(\mathbf{k}_m)$ is the value of $V(\mathbf{k})$ at the reciprocal lattice point $\mathbf{k}_m$. From Eq. 3, P.C. Clapp and S.C. Moss [18] derived the expression for calculating the T_c for Cu_3Au and $CuAu_3$ alloys written as:

$$T_c = \frac{3V_1}{2k_B}\left(1 - \frac{3V_2}{2V_1} + 2\frac{V_3}{V_1}\right). \tag{4}$$

This expression is identical to the critical temperature derived in the above-mentioned way by J.M. Cowley for Cu_3Au [15]. For the CuAu alloy the similar expression has form:

$$T_c = \frac{2V_1}{k_B}\left(1 - \frac{3V_2}{2V_1} + 2\frac{V_3}{V_1}\right), \tag{5}$$

where V_1, V_2 and V_3 are pairwise interatomic potentials on the first three shells.

The improved statistical mechanical approximation developed by R.A. Tahir-Khelli [19] is applied to the analysis of published experimental data on the short-range order parameters in, and the diffuse scattering intensities from, the three stoichiometric copper-gold binary alloys Cu_3Au, CuAu and $CuAu_3$. From this analysis, the corresponding pairwise interatomic potentials extending up to the third nearest neighbor separation are determined. Using a plausible interpolation procedure, pairwise interatomic potentials are estimated for all compositions in the range Cu_3Au to $CuAu_3$ for three stoichiometric compositions. Finally, using these estimates, the variation of the magnitude of the order-disorder transition temperature T_c is predicted as function of the system concentration. The agreement of the theoretical predictions with experimental data of T_c is found be excellent in the range Cu_3Au to CuAu and, in particular, the observed minimum in T_c for the composition $Cu_{0.64}Au_{0.36}$ is faithfully reproduced. While calculating the dependence of the critical temperature T_c on the Cu-Au alloy composition, authors of work [19] and J. M. Cowley [15] implemented the assumption that the value of T_c for stoichiometric compositions of Cu_3Au and CuAu should have an exact maximum. They also noted the need to take into account the pairwise interaction at an interatomic distance further than the third neighbor.

The aim of this work is to calculate the critical temperatures of Cu_3Au, CuAu and $CuAu_3$ alloys using experimental values of short-range order parameters determined from X-ray diffuse scattering intensity, and to compare the results of calculation with data from the phase diagram of the Cu-Au system.

Theory

The Fourier transform of the pairwise interatomic potential $V(\boldsymbol{k})$ for the face centered cubic lattice has form [20]:

$$V(\boldsymbol{k}) = \sum_{lmn} V_{lmn} \cos(\pi l h_1)\cos(\pi m h_2)\cos(\pi n h_3), \qquad (6)$$

where l,m,n are integers for representing the position vector $\boldsymbol{r}(lmn) = \frac{1}{2}l\boldsymbol{a}_1 + \frac{1}{2}m\boldsymbol{a}_2 + \frac{1}{2}n\boldsymbol{a}_3$ of the atom in the node of the lattice, and $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ are the cubic axes. The continuous vector $\boldsymbol{k} = h_1\boldsymbol{b}_1 + h_3\boldsymbol{b}_2 + h_3\boldsymbol{b}_3$ is represented by continuous variables h_1, h_2, h_3 and three vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, $\boldsymbol{b}_3$ are reciprocals to the $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$.

In Cu$_3$Au, CuAu, CuAu alloys, at the reciprocal space point $\boldsymbol{k}_m(1; 0; 0)$ there is a minima $V(\boldsymbol{k}_m)$ corresponding to the maximum of $\alpha(\boldsymbol{k})$ at the critical temperature T_c [18]. Therefore, we have substituted the coordinates $h_1 = 1$, $h_2 = 0$, $h_3 = 0$ into Eq. 6 and obtained following expression:

$$V(\boldsymbol{k_m}) = -4V_1 + 6V_2 - 8V_3 + 12V_4 - 8V_5 + 8V_6 - 16V_7 + 6V_8 - 4V_9 - 8V_{10} + 24V_{11}.$$

Taking into account Eq. 3, we have obtained the expression for critical temperature in the case of alloys with face-centered cubic structure:

$$T_c = -\frac{2c_A c_B}{k_B}(-4V_1 + 6V_2 - 8V_3 + 12V_4 - 8V_5 + 8V_6 -$$
$$-16V_7 + 6V_8 - 4V_9 - 8V_{10} + 24V_{11}). \qquad (7)$$

Using this expression, by comparing the calculated value of the critical temperature with the corresponding experimental value, it is possible to estimate the reliability of the values of the pairwise interaction potential, as well as the experimental values of the short-range order parameters, through which the pairwise interaction potential is calculated. Note, that it is possible to derive Eq. 7 from Eq. 1 according to paper [15].

Results of Calculations and Discussion

Using Eq. 2 and Eq. 6, it is possible to compute $\alpha(\boldsymbol{k})$ by varying the values of V_i, and then calculating the theoretical values of $\alpha(R_i)$ where R_i is radius of the i-th shell. The required values of V_i are those that correspond to the theoretical values of $\alpha(R_i)$ closest to the experimental values of $\alpha(R_i)$; that is, the following condition was achieved:

$$\langle \Delta^2 \rangle_{min} = \sum_i^N [\alpha_i(\text{theor.}) - \alpha_i(\text{exper.})]^2,$$

where N is number of counted shells.

Using this method, we computed the values of pairwise interaction potentials in Cu$_3$Au and CuAu$_3$ alloys. The normalization constant in Eq. 2 was chosen as $C=1$. In the computation of pairwise interaction potential, in the first eleven shells of the Cu$_3$Au alloy we applied values of short-range order parameters, which were obtained by S.C.Moss [4] and are shown in Table 1. In this work, we obtained values of potential in the first two shells that were comparable with results $V_1/k_B = 336.1$ K and $V_2/k_B = -77.3$ K of previous work [18], but differ from other results $V_1/k_B = 223.2$ K and $V_2/k_B = -247.7$ K [19]. We have calculated ratios $V_2/V_1 = -0.185$ and $V_3/V_1 = 0.030$, which are comparable with $V_2/V_1 = -0.208$ and $V_3/V_1 = 0.027$ calculated in other work [21] applying short-range order parameters of the CuAu$_3$ alloy adopted from a previous paper [4]. The set of V_i –s obtained in this work was applied in the estimation of critical temperature T_c in Cu$_3$Au alloys via Eq. 1. The result of this estimation is shown in the last row of Table 1 in comparison with experimental values of T_c [14]. We can conclude that the calculated T_c value for Cu$_3$Au in this work, is in good coincidence with corresponding experimental result.

Table 1. Values of short-range order parameters α_i, pairwise interaction potentials V_i and critical temperatures T_c of Cu-Au alloys

i	Cu$_3$Au		CuAu		CuAu$_3$	
	α_i [4]	V_i/k_B (K)	α_i [2]	V_i/k_B (K)	α_i [3]	V_i/k_B (K)
1	-0.195	331.4	-0.118	126.4	-0.06	78.5
2	0.215	-61.4	-0.002	-4.1	0.20	-95.5
3	0.003	9.84	0.000	-142.7	-0.08	70.0
4	0.077	-3.8	0.050	-168.9	0.14	-1.0
5	-0.052	17.3	-0.030	-25.3	0.01	-3.0
6	0.028	-8.5	0.030	-176.9	0.03	0.7
7	-0.010	-1.2	-0.020	-70.2	-0.04	1.5
8	0.036	17.2	0.000	24.2	0.02	10.5
9	-0.015	-5.1				
10	0.007	11.8				
11	0.015	10.4				
	Calc. T_c=664 K Exp. T_c=663 K [14]		Calc. T_c=680 K Exp. T_c=683 K [14]		Calc. T_c=521 K Exp. $T_c \approx$470K [14]	

In the case of the CuAu$_3$ alloy, the calculation of pairwise interaction potential on the first eight shells was conducted using corresponding short range-order parameters defined experimentally in previous work [3] (see Table 1). Values of pairwise interaction potential on the first three shells calculated in this work are comparable with the corresponding values V_1/k_B=68.6 K, V_2/k_B = −82.3 K, and V_3/k_B= 61.7 K, which were obtained in previous work [19] using the Clapp-Moss scheme [18]. The estimated value of T_c is 1.1 times higher than that of the corresponding experimental value [14] (see Table 1).

The computation of pairwise interaction potential on the first eight shells of the CuAu alloy was carried out by the solution of Cowley equations Eq. 1 via the least squares method, using the set of short-range order parameters published previously [2]. In this work, the computed pairwise potential in the first shell of the CuAu alloy is 1.34 times higher than V_1/k_B= 94.1 K previously published [19]. The magnitudes of pairwise interaction potential in the second and third shells are not consistent with the corresponding results of previous works [18,19]. The result of estimating the critical temperature T_c of CuAu is shown in the last row of Table 1. The estimated value of T_c is in good agreement with corresponding experimental data [14].

From the analysis of data in Table 1, we can conclude that the magnitude of the pairwise interaction potential on the first shell in the Cu-Au alloy decreases with increasing gold concentration. A similar tendency has also been revealed in previously reported work [19]. This finding can be explained by a decrease in the magnitude of the short-range order parameter on the first shell with increasing gold concentration in the Cu-Au alloy.

Conclusion

The possibility of calculating the critical temperatures of the order-disorder phase transition in a Cu-Au alloy using the experimental values of the short-range order parameters is shown. In calculating the pairwise interaction potentials of the Cu$_3$Au, CuAu, and CuAu$_3$ alloys, the

Krivoglaz-Clapp-Moss approximation and Cowley equations successfully were applied. An extension of expression for estimation of critical temperature up to eleven shells allows to predict order-disorder phase transition temperatures in Cu-Au alloys with stoichiometric compositions. Calculation of the pairwise interaction potential of the alloy from the experimental set of the short-range order parameters makes it possible to verify the theoretical models for calculating the pairwise interaction potential in binary alloys.

Acknowledgement

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