Electronic Supplementary Information

Cluster expansion Monte Carlo study of Indium-Aluminum segregation and homogenization in $CuInSe_2$-$CuAlSe_2$ pseudobinary alloys

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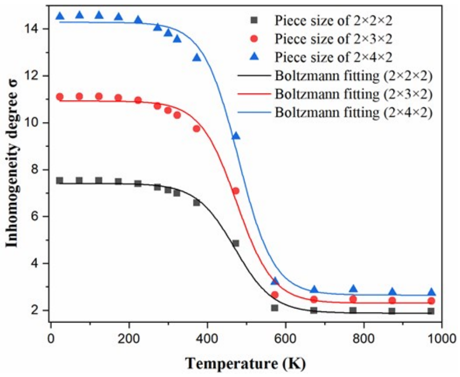

Fig. S1. The dependence of inhomogeneity degree σ on the piece size for the $CuIn_{0.5}Al_{0.5}Se_2$ alloys annealed at different temperatures.

As shown in Fig. S1, the inhomogeneity degree σ depends on the piece size, because the calculation of σ is a statistical method. The reason why we chose a piece size of 2×2×2 is mainly based on the following considerations. Firstly, seven concentrations of Al atoms (x = 12.5%, 25.0%, 37.5%, 50.0%, 62.5%, 75.0% and 87.5%) for the CIAS alloy have been studied in this work. In order to meet the requirement of various Al contents we studied, the number of active atoms (In-Al atoms) in each piece must be integral multiples of 8 rather than an arbitrary number. For a piece size of 2×2×2, there are 16 active atoms in each pieces. Therefore, the number of active atoms in these 2×2×2 pieces is suitable. Moreover, the same number of active atoms in each pieces has also been used by Ludwig *et al.* to study the phase segregation behavior and the inhomogeneity of In-Ga distributions in $CuIn_{1-x}Ga_xSe_2$ alloys (*Physical Review Letters*, 105, 025702, 2010). Cutting the simulation cells into pieces with 16 active atoms, both we and Ludwig *et al.* have obtained proper results. Secondly, for MC simulation cells with the same size and different Al contents, it is critical that they have to be cut into same number of pieces with the same piece size, in order to make their σ to be comparable. This is able to avoid statistical errors of σ induced by using different piece numbers or sizes. Thirdly, the σ value is not unique even for a given CIAS simulation cell when different piece sizes are used, as shown in Fig. S1 herein. It is hard to tell which piece size can give a better σ for the same CIAS simulation cell, since the σ values from different piece sizes are not comparable for a finite-sized simulation cell. As long as the σ can properly describe the inhomogeneity of In-Al distributions for all considered CIAS alloys, some other piece sizes could also be employed. Although the σ value from different piece sizes may change, one should keep using the same piece size or the same number of pieces for all considered CIAS simulation cells.

Table S1 Parameters of effective cluster interactions (ECIs) for $CuIn_{1-x}Al_xSe_2$ pseudobinary lattice. The empty, point, pair, triplet, and quadruplet clusters are labelled as $J(0,1)$, $J(1,1)$, $J(2,n)$, $J(3,p)$, and $J(4,q)$, respectively, where $n = 1\ldots53$, $p = 1\ldots15$, $q = 1,2$. Coordinates of sites in the cluster are in fraction of lattice vectors. Cluster size is defined as the longest distance between any two sites in the cluster. 188 ordered structures with a maximum of 56 atoms in the supercell have been used in the current cluster expansion fit which yields a satisfactory cross validation score (CVS) of 0.614 meV.

Cluster	Coordinates	Size (Å)	Multiplicity	ECI (meV/cluster)
$J(0,1)$			1	53.592
$J(1,1)$	(0.50,0.50,0.00)		2	1.467
$J(2,1)$	(0.50,0.50,0.00) (0.00,0.50,-0.25)	4.167323	4	5.716
$J(2,2)$	(0.50,0.50,0.00) (0.50,1.50,0.00)	5.874337	4	-3.615
$J(2,3)$	(0.50,0.00,0.25) (0.00,-1.00,0.50)	7.202390	8	-1.548
$J(2,4)$	(0.50,0.50,0.00) (1.00,1.00,-0.50)	7.225815	8	-0.915
$J(2,5)$	(0.50,0.00,0.25) (-0.50,-1.00,0.25)	8.307568	4	2.824
$J(2,6)$	(0.50,0.00,0.25) (0.50,-1.50,0.00)	9.294206	4	-0.978
$J(2,7)$	(0.50,0.00,0.25) (0.50,-0.50,1.00)	9.342566	4	-0.934
$J(2,8)$	(0.50,0.00,0.25) (-1.00,-1.00,0.50)	10.995003	8	-0.296
$J(2,9)$	(0.50,0.00,0.25) (-1.00,-0.50,-0.25)	11.010362	8	-0.163

J(2,10)	(0.50,0.50,0.00) (-1.00,0.00,-0.50)	11.010362	8	-0.252
J(2,11)	(0.50,0.00,0.25) (-0.50,-0.50,1.00)	11.035913	8	0.194
J(2,12)	(0.50,0.00,0.25) (-1.50,0.00,0.25)	11.748675	4	-0.951
J(2,13)	(0.50,0.00,0.25) (0.50,0.00,-0.75)	11.825139	2	-0.236
J(2,14)	(0.50,0.00,0.25) (0.00,-2.00,0.50)	12.465871	8	-0.548
J(2,15)	(0.50,0.00,0.25) (0.50,-1.50,1.00)	12.501968	4	1.008
J(2,16)	(0.50,0.00,0.25) (-1.50,1.00,0.25)	13.135418	4	-0.392
J(2,17)	(0.50,0.50,0.00) (-1.50,1.50,0.00)	13.135418	4	-1.090
J(2,18)	(0.50,0.00,0.25) (-0.50,0.00,1.25)	13.203854	8	-0.754
J(2,19)	(0.50,0.00,0.25) (-1.00,-1.50,0.75)	13.792888	8	-0.434
J(2,20)	(0.50,0.00,0.25) (1.50,-1.50,1.00)	13.813293	8	-0.251
J(2,21)	(0.50,0.00,0.25) (-0.50,-1.00,1.25)	14.451629	8	0.196
J(2,22)	(0.50,0.00,0.25) (-1.00,-2.00,0.50)	14.980441	8	0.007
J(2,23)	(0.50,0.00,0.25) (0.50,-2.50,0.00)	14.980441	4	-0.691
J(2,24)	(0.50,0.00,0.25) (-1.50,0.50,1.00)	15.010493	8	-0.151
J(2,25)	(0.50,0.00,0.25) (0.00,0.00,1.50)	15.070416	4	-0.187
J(2,26)	(0.50,0.00,0.25) (-0.50,-2.50,0.00)	16.091036	8	-0.196
J(2,27)	(0.50,0.50,0.00) (0.00,3.00,0.50)	16.101535	8	-0.287
J(2,28)	(0.50,0.50,0.00) (3.00,0.00,0.50)	16.101535	8	-0.573
J(2,29)	(0.50,0.00,0.25) (0.00,-1.00,1.50)	16.174835	8	-0.132
J(2,30)	(0.50,0.00,0.25) (-1.50,-2.00,0.25)	16.615135	4	0.558
J(2,31)	(0.50,0.00,0.25) (-1.50,0.00,1.25)	16.669291	8	0.506
J(2,32)	(0.50,0.00,0.25) (0.50,-2.50,1.00)	17.156065	4	-0.110
J(2,33)	(0.50,0.00,0.25) (-1.50,-1.50,1.00)	17.156065	8	-0.056
J(2,34)	(0.50,0.50,0.00) (-1.00,0.50,-1.25)	17.208519	4	-0.291
J(2,35)	(0.50,0.00,0.25) (-2.50,0.00,0.25)	17.623012	4	-0.174
J(2,36)	(0.50,0.00,0.25) (-1.50,1.00,1.25)	17.674080	8	0.033
J(2,37)	(0.50,0.50,0.00) (-1.50,1.50,1.00)	17.674080	8	0.055

J(2,38)	(0.50,0.50,0.00) (0.00,-2.50,-0.25)	18.109035	8	-0.010
J(2,39)	(0.50,0.00,0.25) (-2.00,-1.50,-0.25)	18.118364	8	0.141
J(2,40)	(0.50,0.50,0.00) (-2.00,-1.00,-0.50)	18.118364	8	0.000
J(2,41)	(0.50,0.00,0.25) (-0.50,-2.50,1.00)	18.133902	8	-0.021
J(2,42)	(0.50,0.00,0.25) (-1.00,-1.00,1.50)	18.183536	8	0.283
J(2,43)	(0.50,0.00,0.25) (0.00,-0.50,-1.25)	18.217580	8	-0.169
J(2,44)	(0.50,0.00,0.25) (-2.50,-1.00,0.25)	18.576286	4	-0.709
J(2,45)	(0.50,0.50,0.00) (-2.50,-0.50,0.00)	18.576286	4	0.000
J(2,46)	(0.50,0.50,0.00) (-2.00,2.50,-0.25)	19.037988	8	-0.164
J(2,47)	(0.50,0.00,0.25) (1.00,-2.00,1.50)	19.108867	8	-0.035
J(2,48)	(0.50,0.00,0.25) (-1.00,-3.00,0.50)	19.923675	8	-0.361
J(2,49)	(0.50,0.00,0.25) (-2.50,-0.50,1.00)	19.946280	8	-0.363
J(2,50)	(0.50,0.00,0.25) (-1.00,-0.50,1.75)	20.022385	8	0.043
J(2,51)	(0.50,0.50,0.00) (-1.00,0.00,1.50)	20.022385	8	0.000
J(2,52)	(0.50,0.00,0.25) (-1.50,-2.00,1.25)	20.393544	8	-0.176
J(2,53)	(0.50,0.00,0.25) (-3.00,0.00,0.50)	20.771631	4	-0.792
J(3,1)	(0.50,0.50,0.00) (0.50,1.00,0.25) (0.50,1.50,0.00)	5.874337	4	0.286
J(3,2)	(0.50,0.00,0.25) (0.00,0.00,0.50) (0.00,-1.00,0.50)	7.202390	8	-0.107
J(3,3)	(0.50,0.00,0.25) (-0.50,0.00,0.25) (0.00,-1.00,0.50)	7.202390	8	0.050
J(3,4)	(0.50,0.00,0.25) (1.00,0.00,0.50) (1.00,-1.00,0.50)	7.202390	8	0.054
J(3,5)	(0.50,0.50,0.00) (0.00,0.50,-0.25) (1.00,1.00,-0.50)	7.225815	8	-0.215
J(3,6)	(0.50,0.50,0.00) (1.00,0.50,-0.25)	7.225815	8	-0.063

	(1.00,1.00,-0.50)			
J(3,7)	(0.50,0.50,0.00) (0.50,1.50,0.00) (1.00,1.00,-0.50)	7.225815	8	-0.177
J(3,8)	(0.50,0.50,0.00) (1.50,0.50,0.00) (1.00,1.00,-0.50)	7.225815	8	0.000
J(3,9)	(0.50,0.50,0.00) (0.00,1.50,-0.25) (1.00,1.00,-0.50)	7.225815	8	0.048
J(3,10)	(0.50,0.00,0.25) (1.00,0.00,0.50) (0.00,-0.50,0.75)	7.225815	8	0.101
J(3,11)	(0.50,0.00,0.25) (0.00,0.00,0.50) (-0.50,-1.00,0.25)	8.307568	8	-0.122
J(3,12)	(0.50,0.00,0.25) (0.50,-0.50,0.00) (-0.50,-1.00,0.25)	8.307568	8	-0.036
J(3,13)	(0.50,0.00,0.25) (-0.50,0.00,0.25) (-0.50,-1.00,0.25)	8.307568	8	0.010
J(3,14)	(0.50,0.00,0.25) (0.00,-0.50,0.75) (-0.50,-1.00,0.25)	8.307568	4	0.045
J(3,15)	(0.50,0.00,0.25) (0.00,-0.50,-0.25) (-0.50,-1.00,0.25)	8.307568	4	0.000
J(4,1)	(0.50,0.00,0.25) (0.00,0.00,0.50) (-0.50,0.00,0.25) (0.00,-1.00,0.50)	7.202390	8	-0.090
J(4,2)	(0.50,0.00,0.25) (0.00,0.00,0.50) (0.50,-1.00,0.25) (0.00,-1.00,0.50)	7.202390	4	0.182