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Exact Relations between Triplet Probabilities and Pair Correlations in *AB* Binary Alloys and Ising Spin-$\frac{1}{2}$ Systems

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The probabilities for triplet occupation in an AB binary alloy (or spin one-half Ising magnet) are found to be exactly expressible as linear combinations of the three pair correlations if the configurational energy of the system possesses a certain symmetry. The required symmetry is that the energy be invariant when all A atoms are replaced by B atoms and vice versa (or all spins are flipped). Systems having only pairwise or even particle interactions satisfy this requirement. Roberts's values for the pair correlations in CuAu at various temperatures are used to calculate the probabilities of several triplet configurations. The results are somewhat paradoxical and can probably be attributed to the lack of a size-effect correction in Roberts's data. Equations for the triplet probabilities in alloy compositions other than 50–50 are also given; but these require a fourth parameter, the triplet correlation, which is not yet available experimentally.

SINCE the first detailed measurement by Cowley[1] of the pair correlations [or Warren short-range-order (SRO) parameters] for Cu_3AU, it has become possible to experimentally determine the pair correlations in favorable alloy systems up to distances of the order of tenth nearest neighbors. It has long been known that a knowledge of the alloy composition and the Warren SRO parameter α_{ij} was sufficient to determine the four pair probabilities $P_{ij}{}^{AA}$, $P_{ij}{}^{AB}$, $P_{ij}{}^{BA}$, $P_{ij}{}^{BB}$, and to thus provide a partial description of the atomic arrangement in the alloy. What has not been generally realized is that for the special case of a 50-50 composition alloy, the eight triplet probabilities $P_{ijk}{}^{AAA}$, $P_{ijk}{}^{AAB}$, etc., are also directly determinable from the pair correlations α_{ij}, α_{ik}, and α_{jk} provided that the configurational energy of the alloy is a sum of only even number particle interactions. It is normally assumed that the configurational energy is a sum of pairwise interactions, in which case the equalities to be derived below are valid. Conversely, if it becomes possible to measure triplet correlations (as suggested by Cowley[2]), an observed violation of the equations would indicate the importance of three-particle (or higher odd number) interactions.

We shall use the occupation numbers σ_i to describe any state of the alloy or spin system where $\sigma_i=(+1,-1)$ if site i is occupied by an (A,B) atom or equivalently an (up, down) spin. We will not continue to discuss the spin problem explicitly but it will be understood that all the subsequent arguments apply to the spin problem by replacing (A,B) atoms by (up, down) spins.

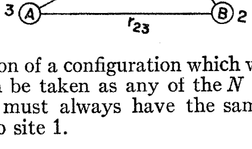

FIG. 1. Illustration of a configuration which would contribute to $P_{123}{}^{ABA}$. Site 1 can be taken as any of the N sites in the crystal but sites 2 and 3 must always have the same orientation and distance relative to site 1.

We note the following useful relations:

$$\sigma_i{}^A\equiv\tfrac{1}{2}(1+\sigma_i)=(1,0) \text{ if an } (A,B) \text{ atom is at site } i,$$

$$\sigma_i{}^B\equiv\tfrac{1}{2}(1-\sigma_i)=(0,1) \text{ if an } (A,B) \text{ atom is at site } i.$$

It is now possible to write definitions for the pair and triplet probabilities in a general form

$$P_{12}{}^{XY}\equiv\sum_\gamma\langle\gamma|\rho(\gamma)\frac{1}{N}\sum_{\tau=0}^{N-1}\sigma_{1+\tau}{}^X\sigma_{2+\tau}{}^Y|\gamma\rangle, \tag{1}$$

$$P_{123}{}^{XYZ}\equiv\sum_\gamma\langle\gamma|\rho(\gamma)\frac{1}{N}\sum_{\tau=0}^{N-1}\sigma_{1+\tau}{}^X\sigma_{2+\tau}{}^Y\sigma_{3+\tau}{}^Z|\gamma\rangle, \tag{2}$$

where X, Y, Z can each be assigned A or B. One of the four possibilities in (1) is $P_{12}{}^{AB}$ which then means the statistically averaged probability that an A-B pair will be found separated by the distance r_{12}. One of the eight possibilities in (2) is $P_{123}{}^{ABA}$ which is the probability that a triangle of sides r_{12}, r_{23}, and r_{31} will be occupied in the manner shown in Fig. 1.

The summation over γ refers to a sum over all the possible individual configurations of the alloy on the N sites of the crystal, there being $N!/(N/2)!^2$ such possibilities for an AB alloy. $\rho(\gamma)$ is the usual thermodynamic weight factor $e^{-\beta H}/\sum_\gamma e^{-\beta H}$. The sum over τ is used to average over all pair sites separated by a fixed distance r_{12} or, in the case of Eq. (2), over all triplet sites which form a triangle of fixed dimensions r_{12}, r_{23}, and r_{31}. The notation $\langle\gamma|\cdots|\gamma\rangle$ merely implies that the value of the quantity inside the brackets is to be calculated for the configuration γ.

As an example, consider the probability $P_{123}{}^{ABA}$ given by Eq. (2) as follows:

$$P_{123}{}^{ABA}=\sum_\gamma\langle\gamma|\rho(\gamma)N^{-1}\sum_{\tau=0}^{N-1}\sigma_{1+\tau}{}^A\sigma_{2+\tau}{}^B\sigma_{3+\tau}{}^A|\gamma\rangle.$$

The product $\sigma_{1+\tau}{}^A\sigma_{2+\tau}{}^B\sigma_{3+\tau}{}^A$ will have the value 1 only if the three sites are simultaneously occupied in the fashion indicated, otherwise the product vanishes. Thus, summing this operator product over τ counts

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[1] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[2] J. M. Cowley, J. Australian Inst. Metals **11**, 258 (1966).

precisely the number of triplets for the γ configuration (out of a possible total of N) that are occupied in the required way. The summation over γ then accomplishes the thermodynamic averaging of all configurations.

We shall now postulate two separate conditions: I: For every configuration γ in the ensemble there exists an inverse $(\bar{\gamma})$ obtained by replacing every A atom by a B atom and vice versa (i.e., all the σ_i's change sign). II: The thermodynamic weight factor has the symmetry property $\rho(\gamma)=\rho(\bar{\gamma})$, i.e., $H(\gamma)=H(\bar{\gamma})$.

Condition I is clearly satisfied for the ensemble of possible configurations of an AB alloy but will not be satisfied for canonical ensembles of other compositions.

A specific example of a Hamiltonian that satisfies condition II would be the general n-particle interaction Hamiltonian

$$H=\sum_{i,j}^{N} V_{ij}\sigma_i\sigma_j+\sum_{i,j,k}^{N} V_{ijk}\sigma_i\sigma_j\sigma_k+\sum_{i,j,k,l}^{N} V_{ijkl}\sigma_i\sigma_j\sigma_k\sigma_l+\cdots, \tag{3}$$

if the terms containing odd numbered products of σ's vanish. The usual pairwise interaction model assumes all but the first term are negligible.

Proceeding to a calculation of the pair and triplet probabilities by using the relations for σ_i^A and σ_i^B in terms of σ_i, and using the notation

$$\langle\sigma_1\sigma_2\sigma_3\rangle\equiv\sum_{\gamma}\langle\gamma|\rho(\gamma)\frac{1}{N}\sum_{\tau=0}^{N-1}\sigma_{1+\tau}\sigma_{2+\tau}\sigma_{3+\tau}|\gamma\rangle,$$

we have

$$P_{12}^{AA}=\tfrac{1}{4}(1+\langle\sigma_1\rangle+\langle\sigma_2\rangle+\langle\sigma_1\sigma_2\rangle).$$

But $\langle\sigma_1\rangle=\langle\sigma_2\rangle=0$, because this is simply the difference in the fraction of A and B atoms in the crystal. Hence, by omission of such terms one has

$$P_{12}^{AA}=\tfrac{1}{4}(1+\langle\sigma_1\sigma_2\rangle), \tag{4a}$$

$$P_{12}^{AB}=\tfrac{1}{4}(1-\langle\sigma_1\sigma_2\rangle), \tag{4b}$$

$$P_{12}^{BA}=\tfrac{1}{4}(1-\langle\sigma_1\sigma_2\rangle), \tag{4c}$$

$$P_{12}^{BB}=\tfrac{1}{4}(1+\langle\sigma_1\sigma_2\rangle). \tag{4d}$$

The pair correlation is simply the Warren short-range-order parameter α_{12} and the equations state the familiar fact that all four pair probabilities depend on a single experimentally determined parameter.[3]

The triplet probability P_{123}^{AAA} becomes

$$P_{123}^{AAA}=\tfrac{1}{8}(1+\langle\sigma_1\rangle+\langle\sigma_2\rangle+\langle\sigma_3\rangle+\langle\sigma_1\sigma_2\rangle+\langle\sigma_2\sigma_3\rangle+\langle\sigma_3\sigma_1\rangle+\langle\sigma_1\sigma_2\sigma_3\rangle)$$

and we note that the triplet correlation $\langle\sigma_1\sigma_2\sigma_3\rangle$ vanishes, because for every contribution to the sum from γ there is an exactly cancelling contribution from $\bar{\gamma}$, i.e., $\rho(\gamma)=\rho(\bar{\gamma})$ but $\langle\gamma|\sigma_1\sigma_2\sigma_3|\gamma\rangle=-\langle\bar{\gamma}|\sigma_1\sigma_2\sigma_3|\bar{\gamma}\rangle$. As a consequence, the eight triplet probabilities can be written entirely in terms of the pair correlations α_{ij} as follows:

$$P_{123}^{AAA}=P_{123}^{BBB}=\tfrac{1}{8}(1+\alpha_{12}+\alpha_{23}+\alpha_{31}), \tag{5a}$$

$$P_{123}^{AAB}=P_{123}^{BBA}=\tfrac{1}{8}(1+\alpha_{12}-\alpha_{23}-\alpha_{31}), \tag{5b}$$

$$P_{123}^{BAA}=P_{123}^{ABB}=\tfrac{1}{8}(1-\alpha_{12}+\alpha_{23}-\alpha_{31}), \tag{5c}$$

$$P_{123}^{ABA}=P_{123}^{BAB}=\tfrac{1}{8}(1-\alpha_{12}-\alpha_{23}+\alpha_{31}). \tag{5d}$$

For the more general situation where either condition I or II or both are violated, $\langle\sigma_1\sigma_2\sigma_3\rangle$ need not be zero and the triplet probabilities now depend on five parameters as follows:

$$P_{123}^{AAA}=\tfrac{1}{8}(1+3c+\alpha_{12}'+\alpha_{23}'+\alpha_{31}'+\tau_{123}), \tag{6a}$$

$$P_{123}^{BBB}=\tfrac{1}{8}(1-3c+\alpha_{12}'+\alpha_{23}'+\alpha_{31}'-\tau_{123}), \tag{6b}$$

$$P_{123}^{AAB}=\tfrac{1}{8}(1+c+\alpha_{12}'-\alpha_{23}'-\alpha_{31}'-\tau_{123}), \tag{6c}$$

$$P_{123}^{BBA}=\tfrac{1}{8}(1-c+\alpha_{12}'-\alpha_{23}'-\alpha_{31}'+\tau_{123}), \tag{6d}$$

$$P_{123}^{BAA}=\tfrac{1}{8}(1+c-\alpha_{12}'+\alpha_{23}'-\alpha_{31}'-\tau_{123}), \tag{6e}$$

$$P_{123}^{ABB}=\tfrac{1}{8}(1-c-\alpha_{12}'+\alpha_{23}'-\alpha_{31}'+\tau_{123}), \tag{6f}$$

$$P_{123}^{ABA}=\tfrac{1}{8}(1+c-\alpha_{12}'-\alpha_{23}'+\alpha_{31}'-\tau_{123}), \tag{6g}$$

$$P_{123}^{BAB}=\tfrac{1}{8}(1-c-\alpha_{12}'-\alpha_{23}'+\alpha_{31}'+\tau_{123}), \tag{6h}$$

where c is the difference in the fraction of A and B atoms, α_{ij}' is the quantity $(1-c^2)\alpha_{ij}+c^2$ and is identical to $\langle\sigma_i\sigma_j\rangle$, and $\tau_{123}\equiv\langle\sigma_1\sigma_2\sigma_3\rangle$. It is apparent that various pairwise combinations of the triplet probabilities can be found that are independent of τ_{123}, but this is not as useful for describing a state of order.

As an application of Eqs. (5a)–(5d), we consider the alloy CuAu. Roberts[4] has measured the α_{ij}'s out to eighth-neighbor separations at several temperatures above T_c. Unfortunately, the α_{ij}'s were not corrected for size effects, which are large in this system as shown explicitly by Borie.[5] Thus, the α_{ij}'s reported by Roberts should not be taken too literally, and we shall use them here primarily for purposes of illustration. They are

TABLE I. Pair correlations (α_i) for CuAu $(T_c=408°\text{C})$.

Neighbor distance, i	Perfect order	Quenched from 500°C	Held at 425°C	Held at 525°C	Perfect disorder
1	$-\frac{1}{3}$	-0.158	-0.123	-0.118	0.000
2	$+1$	$+0.210$	$+0.048$	-0.002	0.000
3	$-\frac{1}{3}$	-0.048	0.00	0.00	0.000
4	$+1$	$+0.153$	$+0.07$	$+0.05$	0.000
5	$-\frac{1}{3}$	-0.050	-0.03	-0.03	0.000
6	$+1$	$+0.093$	$+0.03$	$+0.03$	0.000
7	$-\frac{1}{3}$	-0.035	-0.02	-0.02	0.000
8	$+1$	$+0.070$	$+0.02$	0.00	0.000

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[3] P. C. Clapp and S. C. Moss, Phys. Rev. **142**, 418 (1966).

[4] B. W. Roberts, Acta Met. **2**, 597 (1954).

[5] B. Borie, Acta Cryst. **14**, 472 (1961).

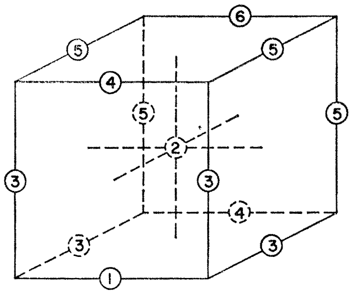

FIG. 2. Sites used for the calculation of triplet probabilities in CuAu.

listed in Table I along with the α_i's for perfectly ordered and perfectly disordered samples.

CuAu is an interesting example to study because the symmetry of the crystal changes from cubic to tetragonal upon ordering. The ordered phase may be described as even-numbered 100 planes of a face-centered cubic lattice occupied by one type of atom and odd-numbered 100 planes occupied by the other type. Since three points are required to define a plane. the triplet probabilities have an advantage over the binary probabilities in that they can provide an answer to the question of whether such layering occurs on a small scale in the disordered state, in anticipation of the ordered structure.

Although we could, in principle, calculate probabilities of any triplet which did not contain a pair separated by more than eighth-neighbor distances, we shall confine our attention to the cluster of sites shown in Fig. 2. All the sites of the cluster are nearest neighbors of site 2, and we shall calculate the triplet probabilities for the case when sites 1 and 2 are occupied by A atoms. Equations (5a) and (5b) yield

$$P_{12j}{}^{AAA}=\tfrac{1}{8}(1+2\alpha_1+\alpha_{1j}),$$

$$P_{12j}{}^{AAB}=\tfrac{1}{8}(1-\alpha_{1j}).$$

In particular we shall calculate the conditional probability $P({}_j{}^B|{}_{12}{}^{AA})$ of a B atom at j given an A atom at 1 and 2, i.e.,

$$P({}_j{}^B|{}_{12}{}^{AA})\equiv\frac{P_{12j}{}^{AAB}}{P_{12j}{}^{AAA}+P_{12j}{}^{AAB}}=\frac{1-\alpha_{1j}}{2+2\alpha_1}.$$

TABLE II. Triplet conditional probabilities $[P({}_j{}^B|{}_{12}{}^{AA})]$ for CuAu.

Cluster site j	Perfect order	Quenched from 500°C	Held at 425°C	Held at 525°C	Perfect disorder
3	1	0.688	0.640	0.634	0.500
4	0	0.469	0.543[a]	0.568[a]	0.500
5	1	0.622	0.570	0.567	0.500
6	0	0.503[a]	0.530[a]	0.539[a]	0.500

[a] Values which are paradoxical in the sense that they do not lie between the perfectly ordered and perfectly disordered values.

Since sites 3, 4, 5, and 6 in Fig. 2 are first, second, third, and fourth neighbors of site 1, we have $\alpha_{13}=\alpha_1$; $\alpha_{14}=\alpha_2$; $\alpha_{15}=\alpha_3$; $\alpha_{16}=\alpha_4$. The calculated values of $P({}_j{}^B|{}_{12}{}^{AA})$ appear in Table II. We see from the column of values for the ordered structure that placing an A atom on sites 1 and 2 resolves the ambiguity of whether the layering occurs on the 100, 010, or 001 planes, in that sites 4 and 6 are forced to contain A atoms, and sites 3 and 5 are forced to have B atoms. If layering also occurs in the disordered state this should appear as a value of less than 0.5 in the table for sites 4 and 6 and a value greater than 0.5 for sites 3 and 5. Only the quenched sample seems to come close to satisfying these conditions. The values in the table marked with a letter are those that do not satisfy the layering condition and we note that although 3 and 5 are preferred B sites in all cases, the paradoxical result emerges that at 425 and 525°C locations 4 and 6 also appear to be preferred B sites.

However, as we noted before, Roberts's results do contain significant errors and he comments that α_2 in particular is probably much too small. Increasing α_2 in our equations would affect only site 4 and change it in the direction of being a preferred A site.

In conclusion, it may be said that the results for CuAu are ambiguous and that a better picture of the disordered state in this system will have to wait for more accurate values of the α_{ij}'s. When such measurements are available for this and other AB alloys, the triplet probabilities should provide a critical test for the importance of higher particle interactions in ordering processes when the direct measurement of triplet probabilities becomes feasible.