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## The number of nearest neighbours of like atoms in the surface layer of binary alloys

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**Abstract.** The number of nearest neighbours of like atoms in an alloyed surface layer is derived from correlation functions of higher order for a square lattice gas with nearest-neighbour attraction and next-nearest-neighbour repulsion. The correlation functions and the position of the phase transition are determined by an extension of the Bethe–Peierls cluster approximation and by Monte Carlo simulation. Qualitative agreement with existing experimental data on the number of nearest neighbours indicates that both interactions are important.

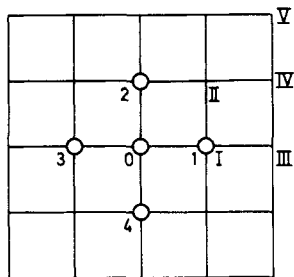
### 1. Introduction

Recently, the method of perturbed angular correlations (PAC) was used to derive the distribution of the number of nearest neighbours of like atoms in a surface alloy of Cu with a few per cent of In (Klas *et al* 1987, 1989). The In atoms, a small fraction of which are radioactive, are deposited on the (100) Cu surface. At temperatures above about 200 K they are believed to penetrate into the surface layer of the Cu crystal, and to occupy regular lattice sites there. In this way a surface alloy is formed. In the PAC measurement a threefold splitting of frequencies was observed. This was interpreted in terms of three different atomic environments of the radioactive In atoms with zero, one or more than one (i.e. two, three or four) other In atoms as nearest neighbours. Following this interpretation, the relative frequency of different numbers of like nearest neighbours of In atoms in the surface alloy was determined. This paper attempts to explain these experimental results by a model calculation for a two-dimensional lattice gas in thermal equilibrium.

We choose a lattice gas on a square lattice with attractive forces between pairs of nearest neighbours and repulsive forces between pairs of next-nearest neighbours. The Hamiltonian of the system is given by

$$H = -V \sum_{\langle i,j \rangle}^{(NN)} n_i n_j + W \sum_{\langle i,j \rangle}^{(NNN)} n_i n_j - \mu \sum_i n_i \quad (1.1)$$

where  $V > 0$  and  $W > 0$  are the interaction energies and  $n_i$  denotes the occupation number (1 or 0) of lattice site  $i$ . In the first term the summation is over nearest-neighbour pairs and in the second one it is over the next-nearest-neighbour pairs, located on



**Figure 1.** The cluster used for the  $5 \times 5$  approximation. The circles mark the sites that are considered for the calculation of the probabilities  $f_i(T)$ . One representative for each set of equivalent sites is denoted by a Roman numeral.

diagonal lines (e.g.  $(0, 0)$  and  $(1, 1)$  in figure 1). Since in the following the grand canonical ensemble is used, the chemical potential  $\mu$  is included in the Hamiltonian.

The probabilities for the different numbers of nearest neighbours can be expressed by static correlation functions of higher order, which we calculate using an extension of the Bethe–Peierls approximation. The approximation used has been tested previously for the case of only repulsive forces between nearest neighbours (Froböse and Jäckle 1985, 1986). It was found that, even in the limiting case of infinitely strong repulsion, this approximation leads to results in good agreement with Monte Carlo simulation. Here we apply the same approximation scheme to the more complicated case of attractive forces between nearest neighbours and repulsive forces between next-nearest neighbours.

In section 2 we present the calculations for a homogeneous single-phase system. Since the phase separation occurring in our model might also be relevant for the interpretation of the experiments, the phase diagram is calculated in section 3. In order to test the quality of our approximations we performed Monte Carlo simulations for the system in the single-phase state for the case of only nearest-neighbour attraction. They are reported in section 4. In section 5 we compare our theory with the experimental data.

Another approach to the problem was given by Dieterich *et al* (1987). They calculated the distribution of the number of nearest neighbours of like atoms by Monte Carlo simulation for a two-dimensional diffusion–reaction model, in which diffusion is governed by cluster kinetics rather than atomic interaction potentials.

## 2. The probability distribution of the number of neighbours

The probability  $f_0$  that some particle (e.g. the particle at site  $0 = (0, 0)$  in figure 1) has no neighbours around it is given by the conditional probability that the sites  $1 = (1, 0)$ ,  $2 = (0, 1)$ ,  $3 = (-1, 0)$  and  $4 = (0, -1)$  are empty if site 0 is occupied. Thus  $f_0$  is given by

$$f_0 = \langle n_0(1 - n_1)(1 - n_2)(1 - n_3)(1 - n_4) \rangle / \langle n_0 \rangle \quad (2.1a)$$

where the angle brackets indicate thermal averages;  $\langle n_0 \rangle$  is the concentration  $c$ . The numerator of the expression (2.1a) can be decomposed into a sum of thermal averages of occupation numbers  $\langle n_i \rangle$ ,  $\langle n_i n_j \rangle$ ,  $\langle n_i n_j n_k \rangle$ ,  $\dots$ ,  $\langle n_0 n_1 n_2 n_3 n_4 \rangle$ , which are, apart from a normalisation factor,  $n$ -particle correlation functions up to fifth order.

Similarly,  $f_1$  is given by the conditional probability that just one nearest-neighbour site  $i$  ( $i = 1, 2, 3, 4$ ) of a particle at site 0 is occupied while the others are vacant; since the probability is the same for each nearest-neighbour site, we obtain

$$f_1 = 4\langle n_0 n_1 (1 - n_2)(1 - n_3)(1 - n_4) \rangle / \langle n_0 \rangle. \quad (2.1b)$$

In the same way all the other probabilities  $f_l$  ( $l = 0, \dots, 4$ ) can be expressed by  $n$ -particle correlation functions.

Since only short-range correlations are involved, a Bethe–Peierls cluster approximation is appropriate. A small cluster consisting of only the centre atom with its nearest neighbours is not sufficient, because the correlations within the second and third coordination shells are relevant for those in the first. Therefore, the approximations were performed for larger square-shaped clusters of lengths 3 and 5 lattice constants, respectively (figure 1). The  $5 \times 5$  cluster was introduced because the smaller cluster might appear not to take into account properly the next-nearest-neighbour interaction. For both cases, the approximations produce satisfactory results, the differences giving an estimate of the errors.

In the present extension of the Bethe–Peierls approximation, the chemical potential at the centre site (0) of the cluster is taken as the bulk chemical potential  $\mu$ , whereas the chemical potential for all the other sites is allowed to be different in order to take into account the effect of the medium surrounding the cluster. It should be noted that for the case of the  $5 \times 5$  cluster one might argue that only the chemical potential at the border sites should be modified, since only these are in contact with the medium. However, since the inner shells of the cluster are also influenced by the surrounding medium, it is reasonable to admit a deviation of the chemical potential for all sites but the centre site. For sites that are equivalent with respect to symmetry, the effective chemical potentials must be equal. This condition reduces the number of parameters. Thus there are only two different effective chemical potentials  $\mu^{(i)}$  and  $\mu^{(ii)}$  for the  $3 \times 3$  cluster and three additional chemical potentials  $\mu^{(iii)}$ ,  $\mu^{(iv)}$  and  $\mu^{(v)}$  for the  $5 \times 5$  cluster.

Within the Bethe–Peierls approximation, the effective chemical potentials  $\mu^{(j)}$  ( $j = i, ii$  and  $j = i, \dots, v$ , respectively) are determined self-consistently in such a way that the occupation probability is the same at all sites of the cluster:

$$\langle n_0 \rangle = \langle n_i \rangle = \langle n_{ii} \rangle \quad (2.2a)$$

for the  $3 \times 3$  cluster, which must be supplemented by

$$\langle n_0 \rangle = \langle n_{iii} \rangle = \langle n_{iv} \rangle = \langle n_v \rangle \quad (2.2b)$$

for the case of the  $5 \times 5$  cluster.

The grand canonical partition function  $Z_{cl}$  of the cluster can be written in the form

$$Z_{cl} = A + Bz \quad (2.3)$$

where  $z$  denotes the bulk fugacity  $\exp[-\mu/(k_B T)]$ .  $A$  and  $B$  depend on all the effective fugacities  $z^{(j)} = \exp[-\mu^{(j)}/(k_B T)]$  but not on  $z$ .  $A$  and  $B$  are evaluated directly by the computer program. For the case of the  $5 \times 5$  cluster the calculations can be simplified considerably by exploiting the symmetry of the cluster. Applying the idea of corner transfer matrices (Baxter *et al* 1980) to this problem, at first a set of partial partition functions is evaluated for the upper-right quarter. Their values depend on the occupation of the sites (0, 0), (1, 0), (2, 0), (0, 1) and (0, 2) (figure 1). Now for a given configuration on the sites (0, 0), (1, 0), (2, 0), (0, 1) and (0, 2) the contribution to the total partition function is obtained as the product of four partial partition functions (one factor for

each quarter), which are selected from the previously computed set according to the occupation of their edges in the present configuration. The summation over all possible configurations, where again symmetry can be used for simplification, yields the total cluster partition function  $Z_{cl}$ .

The occupation probabilities for the single sites of the cluster are obtained as the thermodynamic derivatives of the cluster partition function with respect to  $z$  and  $z^{(j)}$ , respectively. However, these thermodynamic derivatives count the total number of particles on places with the same chemical potential. In order to get the occupation at a single site, the derivatives must be divided by the number of places  $N_j$  that are equivalent because of symmetry. We obtain

$$\langle n_0 \rangle = \frac{z}{Z_{cl}} \frac{\partial Z_{cl}}{\partial z} = \frac{zB}{A + zB} \quad (2.4a)$$

$$\langle n_i \rangle = \frac{z^{(i)}}{N_i Z_{cl}} \frac{\partial Z_{cl}}{\partial z^{(i)}} \quad \langle n_{ii} \rangle = \frac{z^{(ii)}}{N_{ii} Z_{cl}} \frac{\partial Z_{cl}}{\partial z^{(ii)}} \quad (2.4b)$$

for the  $3 \times 3$  cluster, and in addition similar equations for the case of larger clusters.

Using the concentration  $c$  and the temperature  $T$  as independent variables, these equations can be written in the form

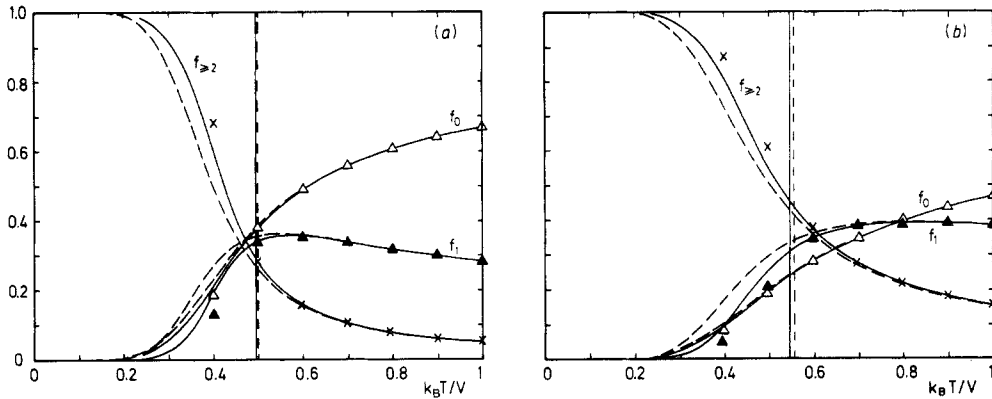
$$z = \frac{c}{1 - c} \frac{A}{B} \quad (2.5a)$$

$$z^{(j)} = N_j c Z_{cl} / (\partial Z_{cl} / \partial z^{(j)}). \quad (2.5b)$$

For low concentrations the fugacities can be calculated from the non-linear equations (2.5) by iteration.

With  $z$  and  $T$  as independent variables instead, a choice that would appear natural from the derivation of the equations, the numerical solution is more difficult because below a certain critical temperature  $T_c$  the solution becomes non-unique as a consequence of the phase transition that the system can undergo. In the numerical treatment this leads to instabilities even at temperatures above  $T_c$ .

In this approximation for the computation of a correlation function  $g(j_1, \dots, j_n) = \langle n_{j_1} \dots n_{j_n} \rangle / c^n$  among  $n$  particles at sites  $j_1, \dots, j_n$  anywhere in the lattice in terms of the fugacities, a set of sites with the same spatial arrangement is selected from the cluster. The correlation function is determined as the sum of the statistical weights of all those configurations of the cluster for which just the selected sites are occupied, divided by the total partition function of the whole cluster and  $c^n$ . Since in this approximation only a distinct part of the whole lattice is considered, translational invariance is not maintained. For this reason different choices of the set within the approximation cluster yield slightly different results for the correlation function. However, for the determination of the probabilities  $f_i$  as defined by equation (2.1), a highly symmetric configuration, a particle embedded in its surroundings, is considered. For this special problem it appears quite natural to locate the set at the middle of the approximation cluster. This ambiguity does not occur in the cluster variation method (Kikuchi and Brush 1967). However, in that approximation scheme the calculations are more involved than in the present paper.



**Figure 2.** The probabilities  $f_l(T)$  for the case of nearest-neighbour attraction only for (a)  $c = 0.04$  and (b)  $c = 0.08$ . Full curves refer to the  $5 \times 5$ , broken curves to  $3 \times 3$  cluster approximation. The vertical lines indicate the transition temperature. Monte Carlo data are included for  $f_0$  ( $\Delta$ ),  $f_1$  ( $\blacktriangle$ ) and  $f_{\geq 2}$  ( $\times$ ).

In the high-temperature regime ( $k_B T \gg V$ ) the interaction between the particles can be neglected. For this case the particles are randomly distributed and  $f_l$  is given by

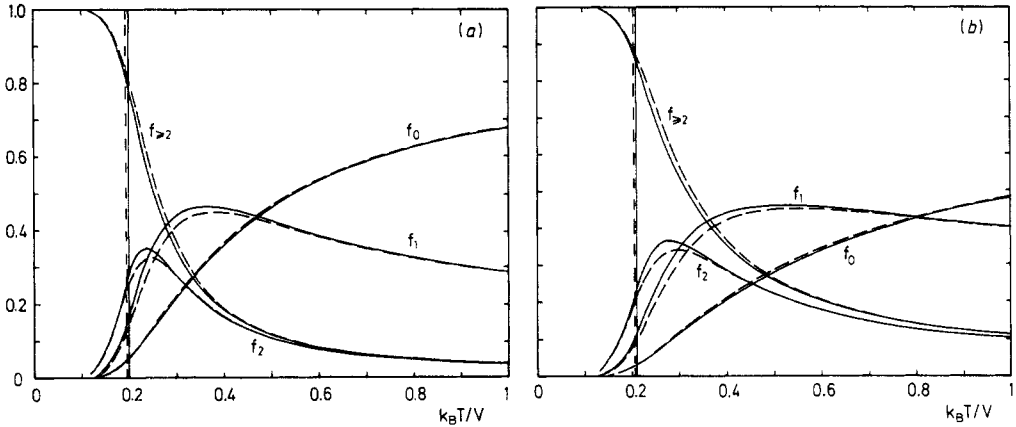
$$f_l = \binom{q_n}{l} c^l (1 - c)^{q_n - l} \quad (2.6)$$

where  $q_n$  is the coordination number for nearest neighbours. For low concentrations,  $c \ll 1$ ,  $f_0$  is largest among the  $f_l$ , which means that the overwhelming part of the particles is isolated.

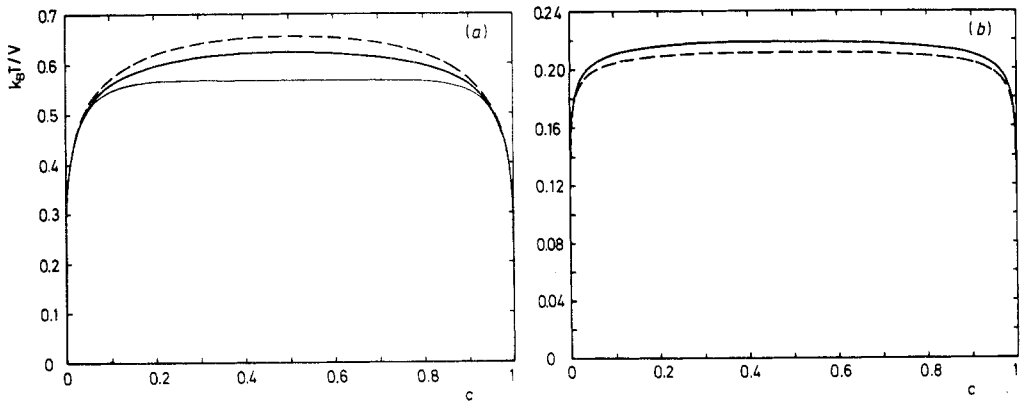
The calculated probabilities  $f_l(T)$  for  $l = 0$  and  $l = 1$  are represented in figures 2(a) and (b) for the case of nearest-neighbour attraction only, and for  $l = 0, 1, 2$  in figures 3(a) and (b) for the case of an additional repulsive interaction  $W = 0.4V$  between next-nearest-neighbour pairs for the concentrations  $c = 0.04$  and  $0.08$ , respectively. In the experiments there is no means for the distinction of the particles having two, three and four nearest neighbours, so that only the sum of their contributions can be measured. Therefore we include  $f_{\geq 2}$ , which is defined as  $f_2 + f_3 + f_4$ . Moreover, the temperatures of the phase transition for these concentrations are marked by vertical lines. Above the phase transition, the approximations for both cluster sizes are in good agreement with each other and also with the data obtained from Monte Carlo simulation.

For the case of negligible interaction at high temperatures, equation (2.6) would yield  $f_0 = 0.85$ ,  $f_1 = 0.14$  and  $f_{\geq 2} = 0.01$  for the concentration  $c = 0.04$ . As can be seen from figure 2(a) at  $k_B T \approx V$  (the maximum temperature considered in the present paper) most of the particles are still isolated but the values found for the probabilities ( $f_0 = 0.67$ ,  $f_1 = 0.28$ ,  $f_{\geq 2} = 0.05$ ) deviate considerably from the high-temperature values as a consequence of the attractive interaction. For the higher concentration of  $c = 0.08$ , the deviations are still larger because the interaction becomes more effective.

The temperature dependence of the probabilities  $f_l$  agrees qualitatively for the lower and the higher concentration, with the only difference being that the influence of the interactions is more pronounced for the higher concentration. When the temperature goes down,  $f_0$  decreases, whereas  $f_1$  varies only slightly. Because of the attractive



**Figure 3.** The probabilities  $f_i(T)$  for the case of nearest-neighbour attraction and an additional next-nearest-neighbour repulsion of  $W = 0.4V$  for (a)  $c = 0.04$  and (b)  $c = 0.08$ . Full curves refer to the  $5 \times 5$ , broken curves to  $3 \times 3$  cluster approximation. The vertical lines indicate the transition temperature.



**Figure 4.** The phase diagram for (a)  $W = 0$  and (b)  $W = 0.4V$ . Full curves refer to the  $5 \times 5$ , broken curves to  $3 \times 3$  cluster approximation. The lower thinner curve in (a) represents the exact phase boundary.

interaction, at lower temperatures the forming of clusters becomes more and more favoured and  $f_{\geq 2}$  grows when the temperature decreases. When the temperature of the phase transition is reached, the system separates into two phases. Even at temperatures slightly below  $T_c$  their concentrations are very near to 0 and 1, respectively, as can be inferred from the phase diagram in figure 4(a). Hence most of the particles are contained in the dense phase and at temperatures sufficiently below  $T_c$  the contribution from particles of the dilute phase can be neglected. Therefore the present approximation is applicable at low temperatures, although homogeneity of the system is supposed for the derivation. In the dense phase all the particles are lumped together, so that most of the particles are surrounded by four neighbours. At such a low temperature, due to the growing of  $f_4$ ,  $f_{\geq 2}$  nearly reaches 1, whereas  $f_0, f_1, f_2$  and  $f_3$  approach 0. For this reason  $f_1$

must show a maximum as a function of  $T$ . The temperature at which  $f_{\geq 2}$  increases considerably is accordingly very near to the critical temperature (exactly,  $k_B T_c = 0.567V$ ).

Taking into account an additional repulsive interaction of  $W = 0.4V$  between next-nearest-neighbour sites shifts the phase transition to lower temperatures by nearly a factor of 3. Since the next-nearest-neighbour interaction is most effective for particles with a nearest-neighbour shell consisting of two or more particles, shells with more than just one particle become more unlikely than surroundings with only one or no particle. Thus the formation of larger clusters is suppressed in comparison with the case of no next-nearest-neighbour interaction. As a result the transition temperature  $T_c$  is reduced and the maximum in  $f_1(T)$  is more pronounced.

### 3. The phase transition

As was mentioned in the previous section, the solution of the equations (2.2) for the effective fugacities  $z^{(j)}$  is not always unique when  $z$  and  $T$  are considered as independent variables. For temperatures below a critical temperature  $T_c$  three different solutions are found for fixed  $z$  and  $T$ , an indication that the system undergoes a phase transition.

When, on the other hand,  $c$  and  $T$  are taken as independent variables, the solution of the equations (2.4) is always found to be unique. However, if we consider  $z$  as a function of  $c$  at fixed  $T$ , it turns out that  $z(c)$  is no longer a monotonic function for temperatures lower than  $T_c$ , as is required by thermodynamic stability, but shows a van der Waals loop instead. This situation is typical for approximations that contain the assumption of finding the same fixed density in every cell of a cluster (Hill 1956 appendix 9). In general, the transition is determined by applying Maxwell's construction to the isotherm using the condition that

$$\int_{c_2}^{c_1} \mu(c) \, dc = \mu(c_1)(c_2 - c_1) = \mu(c_2)(c_2 - c_1) \quad (3.1)$$

where  $c_1$  and  $c_2$  are the densities of the homogeneous 'gas' and the homogeneous 'liquid' phase at equilibrium. For all concentrations within these limits the system is in the mixed two-phase state.

However, in the case of the lattice gas with pair potentials only, the transition can be found much more easily due to the particle-hole symmetry of the lattice gas (Hill 1956 chapter 41, Binder and Kalos 1980). By the transformation  $S_j = 2n_j - 1$  it can be shown that the lattice gas is equivalent to the Ising magnet (occupied sites corresponding to the spin-up state, empty sites to the spin-down state). The quantity  $B = (2\mu + q_N V - q_{NN} W)/4$  plays the role of the external magnetic field, where  $q_N$  and  $q_{NN}$  are the coordination numbers for nearest and next-nearest neighbours, which are both 4 for the square lattice gas. Since the Ising Hamiltonian with pair interaction is symmetric with respect to the simultaneous reversion of all spins and the magnetic field, the lattice gas shares the symmetry properties when particles and holes are exchanged and the chemical potential is replaced by  $-(\mu + q_N V - q_{NN} W)$ . This symmetry property implies the relation for the chemical potential  $\mu$  as a function of  $c$  when  $T$  is fixed:

$$\mu(c) = -\mu(1 - c) - q_N V + q_{NN} W. \quad (3.2)$$

Consequently the isotherm  $\mu(c)$  has a point of symmetry at  $c = 0.5$ ,  $\mu =$



$-(q_N V - q_{NN} W)/2$ . Since in the Bethe–Peierls approximation particle–hole symmetry is preserved, the approximate solution must show up the same symmetry property as the exact solution. Hence the horizontal line in the phase diagram from Maxwell’s construction must pass through this point for equation (3.1) to be fulfilled. Therefore the condition (3.1) may be replaced by the simpler requirement  $\mu = -(q_N V - q_{NN} W)/2$  for the determination of the phase boundary of the lattice gas.

It should be noted, however, that this simplification relies on the fact that only pair potentials are considered in the present paper. The symmetry argument would not apply if interactions of higher order were taken into account.

In the language of the Ising magnet the phase boundary is given by the zero-field magnetisation curve, which is known exactly for the case of nearest-neighbour interaction only. We use it for testing the quality of the approximation for the case  $W = 0$ .

The point of symmetry represents one of three possible solutions for  $T < T_c$ . However, it has no physical meaning. The two other solutions determine  $c_1$  and  $c_2$ , the concentrations at the phase boundaries for a given temperature  $T$ . From equation (3.2) we infer

$$c_1 + c_2 = 1. \quad (3.3)$$

By determining  $c_1$  and  $c_2$  as a function of temperature the phase diagram is obtained. In figure 4(a) the exact phase diagram from the magnetisation curve as found by Onsager and Kaufmann and Yang (Hill 1956) is compared with that obtained by the Bethe–Peierls approximation for both cluster sizes. At temperatures not too near to  $T_c$  ( $T \leq 0.7T_c$ ) or equivalently for concentrations  $c$  with  $c \leq 0.05$  or  $c \geq 0.95$ , respectively, the agreement between the approximate curves and the exact curve is very good. Approaching the critical temperature such a good accordance cannot be expected, because the phase transition becomes more and more of second order in character. Therefore, the importance of the long-range fluctuations, which cannot be treated adequately by such a small cluster, grows when  $T_c$  is approached. With this in mind, a deviation of about 10% from the exact value near to  $T_c$  appears to be acceptable.

When in addition the repulsive next-nearest-neighbour interaction is taken into account, there is no longer an exact solution available. From the observed changes when the cluster size is enlarged from  $3 \times 3$  to  $5 \times 5$  we conclude that the precision will be sufficient in the range of concentrations relevant for the experiments. It is only for the immediate environment of the critical temperature that we expect deviations of the same order of magnitude as in the case without next-nearest-neighbour repulsion.

#### 4. Monte Carlo simulation

The system with nearest-neighbour interaction only was also investigated by Monte Carlo simulations for a square lattice with  $\Omega = 256 \times 256$  sites. Periodic boundary conditions were applied. The temperatures were chosen within the range from  $k_B T = 0.5V$  up to  $1.0V$ . For  $k_B T$  lower than  $0.5V$  some indication for critical slowing down because of the phase transition was observed. An inspection of the particle configurations at these low temperatures showed that the system would correspond to a two-component system with one big cluster and only a few particles around it rather than to a homogeneous system. Therefore, the temperature range was not extended to still lower temperatures.

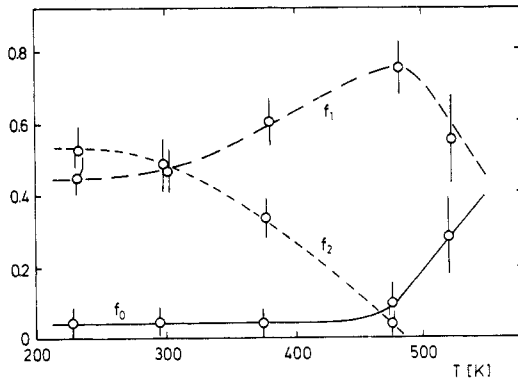


Figure 5. Experimental results as given by Klas *et al* (1987).

The simulations were carried out at a fixed number of particles. According to the desired concentration  $N = c\Omega$  particles were distributed randomly in the lattice to get a starting configuration. The Monte Carlo procedure consisted of choosing randomly a particle and an empty site from the lattice. The gain in energy  $\Delta E$  when the selected particle was moved to the empty state was calculated. When it turned out to be negative, the particle was moved to the new position, otherwise the move was only executed with probability  $\exp[-\Delta E/(k_B T)]$ . After a period of thermalisation, the numbers of like nearest neighbours were periodically evaluated in time intervals of 50 Monte Carlo steps per particle. The averages are represented as symbols in figures 2(a) and (b). The results of the Bethe–Peierls approximation for the  $5 \times 5$  cluster are in full agreement with the Monte Carlo data.

## 5. Comparison with experiment

In this section we compare our results with the experimental data for a sample of a Cu crystal covered by a 7% In surface layer as shown in figure 5 (Klas *et al* 1987). The experimental data and the calculated probabilities show similar behaviour as functions of  $T$  for both cases of  $W = 0$  and  $W = 0.4V$ , respectively. However, the qualitative agreement is significantly better when the additional repulsive next-nearest-neighbour interaction of  $W = 0.4V$  is taken into account. From the comparison of the temperature dependence of the experimental  $f_0$  with our calculations we estimate  $V/k_B$  to  $1700 \pm 200$  K. The experimental probability  $f_1$  shows a relatively high maximum with a value of about 0.75. This cannot be reproduced by the present calculations even when  $W$  is increased. The experimental values for  $f_{\geq 2}$  appear too small compared with the Bethe–Peierls approximation.

## 6. Conclusions

The model calculation presented above shows that the experimental findings of Klas *et al* (1987) can be qualitatively explained by a lattice-gas model with relatively simple atomic interactions. This qualitative agreement lends support to the interpretation of the experimental results by their authors. It shows that both attractive and repulsive interactions are important. The agreement is not quantitative, however. By increasing

the parameter  $W$  of the repulsive interaction between next-nearest neighbours, the agreement between the data and the calculations can still be improved slightly. In the present paper  $W$  was deliberately fixed at  $0.4V$ , since for  $W > 0.5V$  new phases become stable at sufficiently low temperatures and the phase diagram becomes more complex. The discrepancies between the calculated and the measured temperature dependences of the distribution of the number of like atoms may be due to the existence of more complicated atomic interactions as compared with the present model.

Since in our model phase separation occurs at low temperatures, it would be interesting to explore the equilibrium properties of the surface alloy at temperatures below 200 K by very slow cooling.

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