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STATISTICAL ANALYSIS OF THE EARLY STAGES OF PHASE DECOMPOSITION BY ATOM PROBE

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Abstract - The statistical methods for detection and characterization of solute clustering and ordering have been examined both in actual atom probe experiments and with the use of Monte-Carlo computer simulations. The results have indicated that whereas the Hetherington and Miller mean separation method is more appropriate to detect clustering, the Johnson and Klotz order parameter method is required to detect short range order in concentrated solid solutions.

1. INTRODUCTION

Clustering, short range ordering (SRO), and the initial and early stages of phase decomposition are important regimes in the understanding of phase transformations. Since their scale approaches atomic dimensions, experimental characterization of these reactions is singularly difficult. The direct measurement of local chemical compositions with the atom probe can therefore be particularly useful in these studies. In this paper, some statistical techniques for interpreting atom probe experiments are examined. The data chain obtained from the atom probe is a one-dimensional representation from the deconstruction of a three-dimensional material. The aim of any analysis is to study the relationship between the one-dimensional and three-dimensional structures.

It must be emphasized that neighboring atoms in the atom probe data chain are not necessarily nearest neighbors in the crystal. Even in the special case where the effective diameter of the probe aperture is set to collect atoms from a cylinder equivalent to a single atom diameter, the less than ideal detector efficiency and the presence of trajectory aberrations violate the nearest neighbor condition. In this case, it is probable that some atoms in the defined geometric cylinder are not collected and some additional atoms from outside the defined area are captured. In the more general case, where the effective probe aperture defines a larger area on the surface, the neighbors in the atom probe data chain may originate at least as far apart as the effective probe diameter.

1.1 MARKOV CHAIN ANALYSIS

The assumption that the one-dimensional representation is a Markov chain has been proposed as a starting point of the analysis by a number of authors.^[1-4] The most scholarly approach was the treatment of Johnson and Klotz (J&K).^[1] This approach considers only the number of AA, AB, and BB nearest neighbor pairs in the data chain and does not examine atoms spaced further apart. If clustering is present (i.e. the number of BB pairs is greater than random), the J&K ordering parameter, θ , is larger than 1. Conversely, if short range ordering is occurring (i.e. the number of AB pairs is greater than the random case which is equivalent to the number of BB pairs being less than the random case) the J&K ordering parameter, θ , should lie between 0 and 1. The significance of the experimental ordering parameter should be compared to the random value with respect to the standard error, τ (i.e. $(\theta-1)/\tau$, where $\tau = \sqrt{[\theta(1-\theta p)(1-2p+\theta p^2)/(p^2(1-2p+\theta p))]/n}$, n is the number of atoms, and p is the solute content of B atoms).

1.2 MEAN SEPARATION

An alternative approach based on the separation of the solute atoms, μ , in the atom probe data chain has been suggested.^[2] The mean separation of any distribution of solute atoms, $\bar{\mu} = (1-p)/p$, depends only on the solute content, p , and is not influenced by the distribution of the solute in the chain. The distribution does however influence the individual separations of solute atoms. The variance of the separations in the experimental data chain may be used to detect deviations from a random distribution when compared to the estimated variance for the random data set. The experimental and estimated variances may be determined from the following expressions: $\sigma_{\text{exp}}^2 = (\sum \mu^2)/N - \bar{\mu}^2$ and $\sigma_{\text{est}}^2 = (1-p)/p^2$, where N is the number of B atoms. A useful parameter to compare to the J&K ordering parameter significance is the difference of the estimated and experimental variances divided by the standard error, τ_{est} , of the estimated variance (i.e. $(\sigma_{\text{exp}}^2 - \sigma_{\text{est}}^2)/\tau_{\text{est}}$; where $\tau_{\text{est}} = \sqrt{q(1+6q+q^2)/p^4/N}$, and $q = 1-p$).

1.3 OTHER APPROACHES

Tsong et al. have attempted to estimate a parameter which indicates clustering.^[3] Some comments on the usefulness of this were raised in a previous paper.^[2] Wang et al. have attempted to extend this analysis.^[4] The critical uncertainty seems to be the physical meaning of their parameter p which is used to estimate the clustering; it is not clear whether it refers to clusters in the alloy or clusters in the data chain.

2. MONTE-CARLO COMPUTER SIMULATIONS

Computer-modeled solid solutions which have been decomposed with a Monte-Carlo algorithm employing a nearest neighbor Ising interaction have been used with the intention of determining strategies for analyzing the earliest stages of precipitation but not to characterize the microstructures in which two distinct phases can be resolved. Three alloy compositions containing 2, 10 and 20% solute have been considered. These were aged for a time of 16 vacancy steps per atom after a deep quench with an attractive Ising interaction between the atoms. The 20% alloy was also given a deep quench and a potential to cause short range ordering. The particle size distributions shown in Fig. 1 demonstrate the type of microstructure produced. The largest clusters in the 2% and 10% alloys contained 14 and 95 atoms, respectively. The volume fraction of the 20% alloy was larger than the percolation limit and a percolated particle containing 1000's of atoms formed. A more detailed discussion of percolated structures will be made in a future paper. All the distributions are sharply peaked at 1 atom per "particle". It should be noted that conventional simulations of atom-probe experiments involving the random placing of spheres of a second phase in a crystal are not realistic for the early stages. The Monte-Carlo method is also likely to be a much better model for the growth and coarsening regimes, especially for alloys with high solute contents. The model used here includes only nearest neighbor interactions; a useful extension would be to consider longer range interactions. The main disadvantage is that it is difficult to include the effects of stress which are known to influence particle size distribution and morphology.

2.1 MONTE-CARLO SIMULATIONS OF CLUSTERING: EFFECTIVE DIAMETER OF PROBE APERTURE

The ordering parameter defined by J&K and the variance of the mean particle separation have been used to characterize the microstructures. The physical meaning of the parameter used by Tsong et al^[3] is not clear and there is insufficient detail in the paper by Wang et al^[4] to be able to apply their analysis. If the experimental conditions have been chosen to ensure that the correct compositions are measured, a remaining variable is the effective diameter of the probe aperture, which can be used to control the number of atoms detected from a layer. A correctly designed experiment will optimize this value with respect to the goals of the experiment. The parameter θ is shown in Fig. 2 as a function of the square root of the number of atoms detected per plane for experiments in which the detector efficiency is assumed to be 1. The value of θ decreases monotonically as the number of atoms detected per plane increases, for all alloy compositions. The values of θ measured directly from the crystal are in agreement with the values obtained from a simulated atom probe experiment in which one atom is detected from a layer. For example, the measured value from the 10% crystal was 3.6 and the atom probe gave a value of 4.00 ± 0.4 . If the goal of an experiment is to estimate the parameter θ , then it is necessary to detect one atom per layer; there is a systematic deviation from this value if larger numbers per layer are detected.

The absolute value of θ may be of secondary interest to investigators who would like merely to compare alloys. In this case, what is required is the most precise estimate of the deviation of θ from the value of 1 expected for a random alloy. The optimum number of atoms detected per plane is not necessarily the same as required for investigating the absolute value of θ ; one could hypothesize that detecting a larger total number of atoms will provide a more accurate estimate of a deviation from random even though the parameter has no simple physical meaning; i.e. the larger number of atoms collected compensating for a decrease in resolution. The significance of the deviation from random, $(\theta-1)/\tau$, is shown in Fig. 3. The maximum value is obtained when the number of atoms per layer approaches 1. Therefore, not only is the correct value of θ obtained when 1 atom per plane is detected, but also the value yields the most precise indication of the deviation from random when normalized to its standard deviation.

In some cases, neither the correct value of the parameter θ nor a comparison of the alloys is of interest but an indication of whether or not clustering has occurred is required. The ratio of the variance of the separation of similar atoms to the value expected from a random alloy is plotted in Fig. 4 against the square root of the number of atoms detected per plane. This value generally decreases with increasing number of atoms. However, the significance of the values, estimated by $(\sigma_{\text{exp}}^2 - \sigma_{\text{est}}^2)/\tau_{\text{est}}$, shown in Fig. 5, goes through a maximum. The position of the maximum is a function of the solute content and increases with decreasing solute content. Therefore, if detection of clustering is the goal of an investigation, the optimum number of atoms per plane is not 1 but some larger number which depends on the solute content and aging conditions and corresponds to the maximum in Fig. 5. It should be noted that the deviation from random is larger for the variance of the separation than the deviation of θ from 1.

2.2 MONTE-CARLO SIMULATIONS OF CLUSTERING: DETECTOR EFFICIENCY

A further parameter that must be taken into consideration is the detector efficiency. Altering the detector efficiency is not a simple task and common sense tells us that increasing the detector efficiency will increase the sensitivity of an atom probe. However, since it is difficult to achieve an efficiency of 1, it is useful to understand the effect of different detector efficiencies. The effect of the detector efficiency on the parameter θ is shown in Fig. 6. The result is at first sight counter-intuitive; θ increases or remains constant with decreasing efficiency apparently suggesting that reducing the detector efficiency will improve the sensitivity of the atom-probe. The paradox is resolved by examining Fig. 7 which shows the ratio of the deviation of θ from the value expected from a random alloy, 1, to τ the error in θ , plotted against the detector efficiency. At low detector efficiencies θ becomes larger but also statistically less significant. In the previous section, three distinct experimental goals were defined. Since in this type of experiment generally more than one atom per layer is being detected, the estimation of the correct value of θ is unattainable. The decrease in the significance of θ at low detector efficiencies indicates that, as expected, the sensitivity increases with increasing efficiency and therefore in an ideal experiment to compare alloys the detector efficiency, not surprisingly, should be 1.

The variance of the mean spacing normalized to the expected value for each composition is shown in Fig. 8. The variance decreases as the detector efficiency decreases as does the significance of the deviation from random shown in Fig. 9. These results indicate that the highest possible detector efficiency is advantageous and also outline the consequences of performing experiments with practically achievable detector efficiencies.

2.3 MONTE-CARLO SIMULATIONS OF ORDERING

The ordering parameter θ as a function of the square root of the number of atoms detected per layer is shown in Fig. 10. The value estimated from detecting one atom per layer is 0.18 ± 0.06 , which is a reasonable estimate of the value obtained directly from the crystal. The significance of the deviation, $(\theta-1)/r$, is shown in Fig. 11. The detection of one atom per layer is the optimum value either to measure the SRO parameter or to estimate a precise parameter to compare the ordering in different alloys, as it was for clustering.

The value of the variance of the separations is shown in Fig. 12. The significance of the deviation of the value from the random value, $(\sigma_{\text{exp}}^2 - \sigma_{\text{est}}^2)/r_{\text{est}}$ (Fig. 13) indicates that this is not a useful parameter for the detection of ordering. Furthermore, the detection of short range ordering is best achieved by collecting one atom per layer in contrast to the result for the detection of clustering, for which a larger number increased the sensitivity. This seems reasonable considering that the estimation of ordering requires the examination of the relationship of nearest neighbors, whereas clusters usually extend over many atoms. The value of θ and the its significance, $(\theta-1)/r$, against detector efficiency are shown in Figs. 14 and 15, respectively. Their behaviors were similar to the clustering cases although their signs were naturally opposite.

2.4 AUTOCORRELATION FUNCTION

The measurement of the autocorrelation function indicated that the distribution of atoms was non-random. However, the positions of the maxima and minima could not be simply related to the microstructure and furthermore were a function of the number of atoms detected per layer.

3. APPLICATIONS TO SELECTED MATERIALS

The above parameters have been determined for a number of experimental atom probe data chains to illustrate the effectiveness of each method. Several different alloy systems were used so that the methods could be evaluated in different regimes. The three groups of experiments were 1) the early stages of clustering and precipitation in a series of thermally aged and neutron irradiated Fe-Cu^[6] and Fe-Cu-Ni alloys, 2) boron clustering in Ni₃Al,^[6] and 3) the progression from a disordered structure through a SRO state to the initial stages of long range order (LRO) in a Ni₄Mo alloy.^[7] The results of these determinations are summarized in Table 1. These results indicate that the mean separation method is more sensitive than the J&K Markov chain analysis in the detection of clustering in the Fe-Cu alloys. Both methods provided similar results in the Ni₃Al boron clustering situation where boron forms small concentrated clusters. In neither of these clustering cases were any false positive results obtained. In the Ni₄Mo SRO case, the J&K method was able to detect the ordering whereas the mean separation method provided false results. In all three materials, the experimental atom probe results were in agreement with the results predicted from the Monte-Carlo simulations.

4. CONCLUDING REMARKS

This paper demonstrates that it is possible to obtain useful information from finer microstructures than have been hitherto considered accessible to the atom-probe. The parameter θ provides a particularly powerful tool for these investigations. When trying to detect clustering it appeared that the variance of the mean separations was more sensitive than θ . It is likely that this reflects its role in detecting rather than parameterizing the distribution. The variance may really be more sensitive than θ for systems in which ramified or diffuse clusters exist. It is therefore suggested that both should be calculated when analyzing data.

The main subject of this paper is the examination of the parameters used for analyzing the early stages of phase decomposition. However, there is a more general methodology to which attention should be drawn; that is the interplay between simulations and experiments. The simulations are used in order to design appropriate experiments; the experimental data can then be fed back to refine the simulations. In this study the microstructures obtained from the decomposition of a crystal by the Monte-Carlo algorithm have not been directly related to the experimental data. However, the results presented here lead to this as the next and obvious step, and this step will help to increase our fundamental understanding of the precipitation process.

Acknowledgments

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TABLE 1. Selected Parameters determined from Atom Probe Experiments
(alloy compositions are quoted in atomic %)

Material	Condition	State	Element	Number of atoms	J&K Parameters		Mean Separation Parameters		
					$\theta \pm r$	$(\theta-1)/r$	σ_{exp}^2	σ_{est}^2	$\frac{\sigma_{\text{exp}}^2 - \sigma_{\text{est}}^2}{r_{\text{est}}}$
Fe-0.8%Cu	1h 950°C, WQ	Solid Solution	Cu	42295	1.9 ± 1.1	0.82	2.8×10^4	2.7×10^4	0.22
Fe-0.8%Cu	19h 465°C	Matrix only	Cu	70538	15.3 ± 7.4	1.93	6.7×10^5	2.7×10^5	<u>6.19</u>
Fe-0.8%Cu	19h 465°C	Precipitates	Cu	67896	19.6 ± 2.9	<u>6.49</u>	1.0×10^6	3.5×10^4	<u>13.5</u>
Fe-0.3%Cu	n-Irradiated	Precipitates	Cu	33174	10.0 ± 0.35	<u>25.7</u>	3.5×10^4	8.2×10^2	<u>492</u>
Fe-0.3%Cu	669h 288°C	Solid Solution	Cu	128266	4.9 ± 3.4	1.15	4.5×10^5	3.5×10^5	1.5
Fe-Cu-Ni	21h 400°C	«Peak Hardness»	Cu	62153	1.2 ± 0.53	0.37	2.1×10^4	1.5×10^4	<u>3.24</u>
Ni-24%Al-0.24%B		Random	B	35521	1.6 ± 1.6	0.39	5.7×10^4	5.8×10^4	-0.09
Ni-25%Al-0.96%B		Clustered	B	24387	7.7 ± 1.6	<u>4.29</u>	1.3×10^4	9.0×10^3	<u>2.48</u>
Ni ₄ Mo	e-Irradiated	Disordered	Mo	9807	0.99 ± 0.04	-0.25	20.4	18.0	<u>2.1</u>
Ni ₄ Mo	15 min 650°C	SRO	Mo	46873	0.96 ± 0.01	<u>-4.0</u>	8.7	8.6	0.5
Ni ₄ Mo	30 min 650°C	SRO+LRO	Mo	14400	0.91 ± 0.04	<u>-2.25</u>	27.2	26.2	0.7

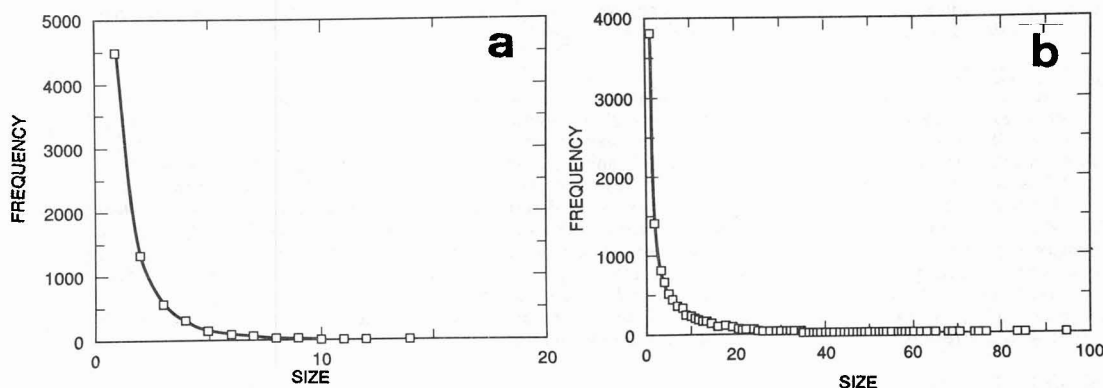


Fig. 1. Particle size distribution after 16 vacancy steps per atom for (a) 2% and (b) 10% solute contents.

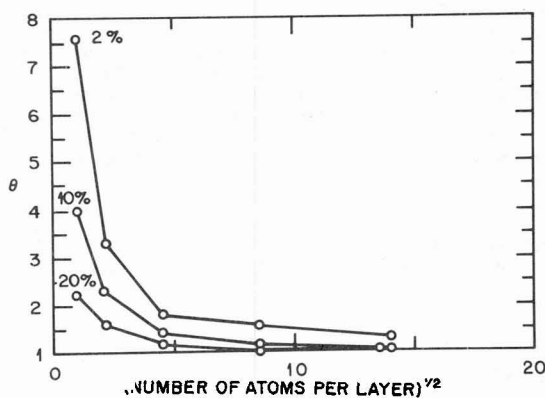


Fig. 2. Variation in the order parameter θ with the number of atoms per layer for 3 different solute contents.

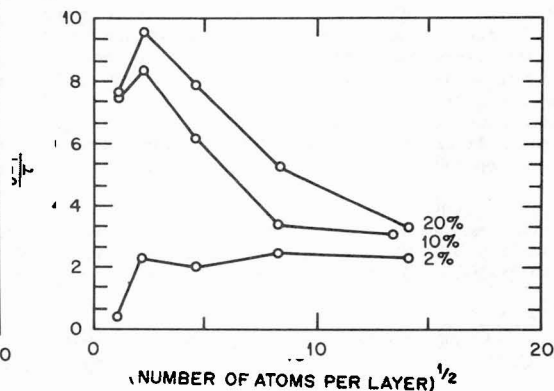


Fig. 3. Difference in order parameter θ from a random solution normalized to the standard deviation for 3 solute contents.

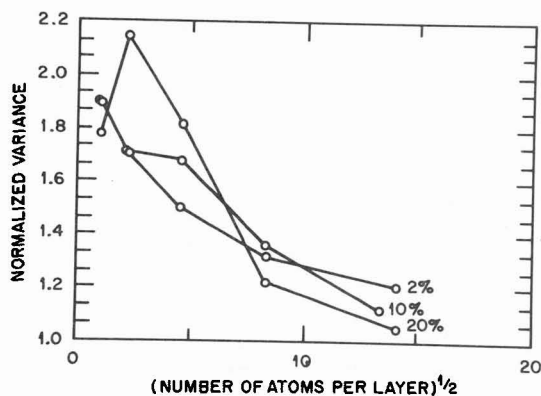


Fig. 4. Variance of the mean separation against number of atoms per layer for 3 solute contents.

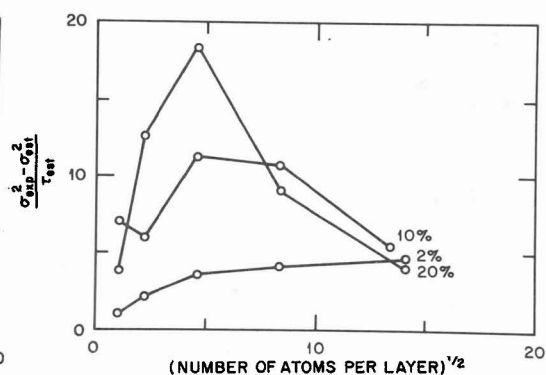


Fig. 5. Difference between the measured and expected variances normalized to the standard deviation against the number of atoms per layer for 3 solute contents.

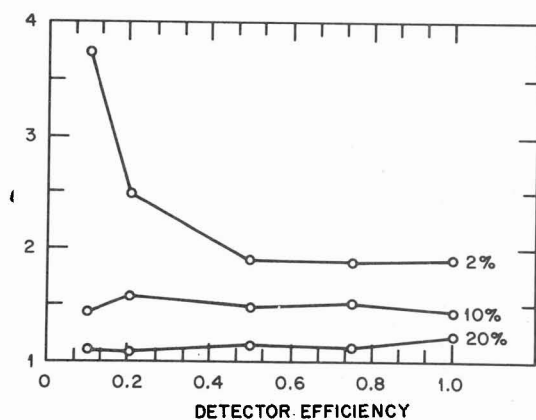


Fig. 6. Variation in the order parameter θ with detector efficiency for 3 different solute contents.

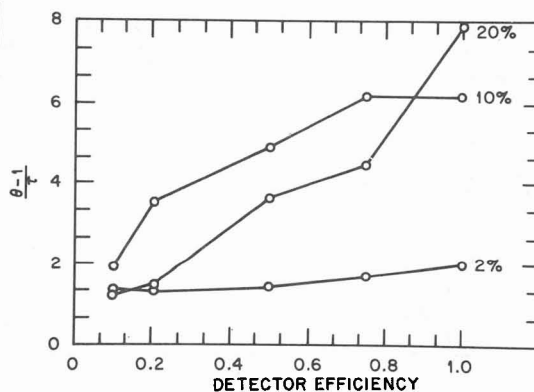


Fig. 7. Difference in order parameter θ from a random solution normalized to the standard deviation against detector efficiency for 3 solute contents.

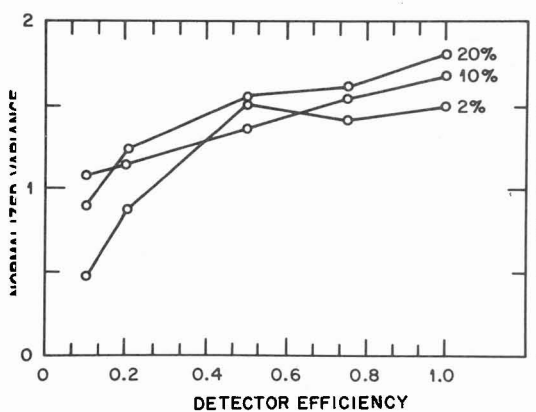


Fig. 8. Variance of the mean separation against detector efficiency for 3 solute contents

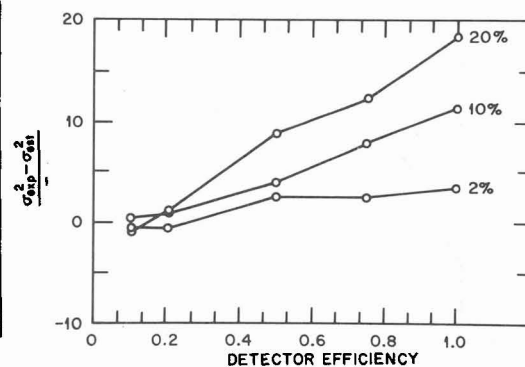


Fig. 9. Difference between the measured and expected variances normalized to the standard deviation against detector efficiency for 3 solute contents.

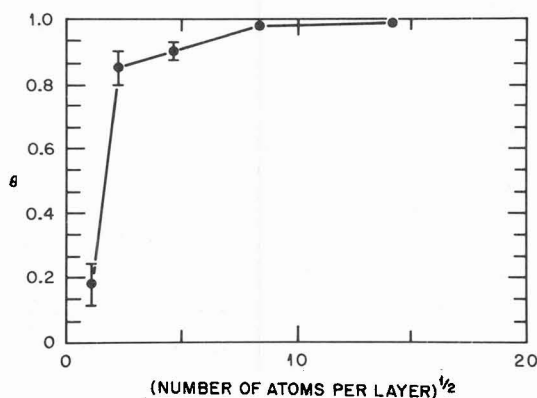


Fig. 10. Variation in order parameter θ with number of atoms per layer for a 20% solute ordered alloy.

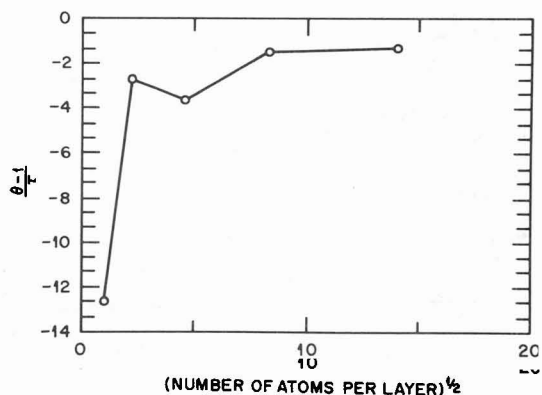


Fig. 11. Difference in order parameter θ from a random solution normalized to the standard deviation against the number of atoms per layer for a 20% solute ordered alloy.

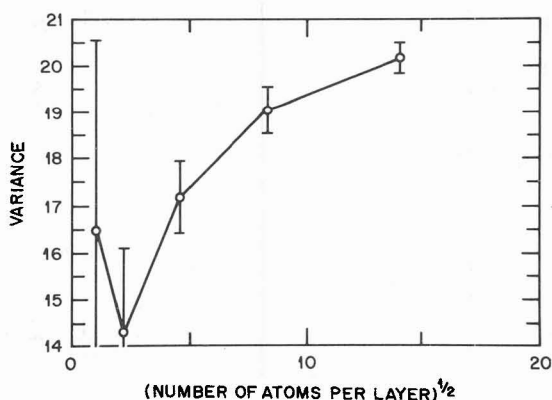


Fig. 12. Variance of the mean separation against the number of atoms per layer for a 20% solute ordered alloy.

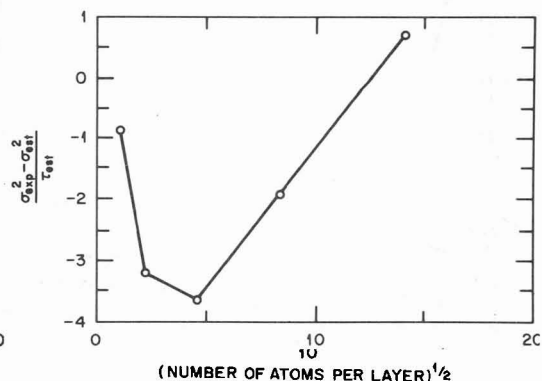


Fig. 13. Difference between the measured and expected variances normalized to the standard deviation against the number of atoms per layer for a 20% solute ordered alloy.

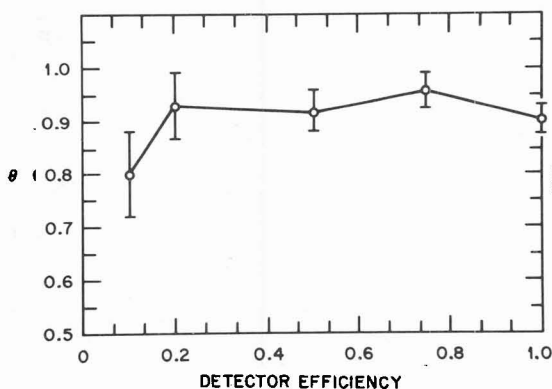


Fig. 14. Variation in order parameter θ against detector efficiency for a 20% solute ordered alloy.

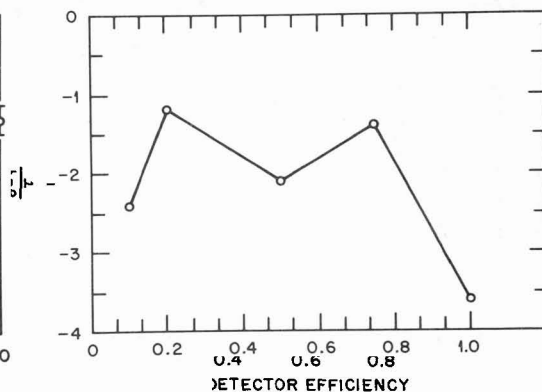


Fig. 15. Difference in order parameter θ from a random solution normalized to the standard deviation against the detector efficiency for a 20% solute ordered alloy.