

- INOUE, S. T. & YAMASHITA, J. (1973). *J. Phys. Soc. Jpn.* **35**, 677–683.
- MACKAY, K. J. H. & HILL, N. A. (1963). *J. Nucl. Mater.* **8**, 263–264.
- PRICE, P. F., HANSEN, N. K. & COPPENS, P. (1977). *ACA Progr. Abstr. Ser. 2*, **5**, 28.
- STEVENS, E. D. & COPPENS, P. (1976). *Acta Cryst.* **A32**, 915–917.
- STEWART, R. F. (1977). *Acta Cryst.* **A33**, 33–38.

Acta Cryst. (1978). **A34**, 65–73

Modeling of Face-Centered Cubic Solid Solutions*

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A computer program has been written to simulate binary face-centered cubic solutions by interchanging the atoms until the populations in 18 shells are in agreement with the short-range order parameters obtained from diffuse X-ray measurements. Comparisons are made between the intensity maps from the model and from the data for most of the published work. We conclude that the published data are of reasonable quality, although sometimes the alphas are somewhat too large or the intensity maps contain artifacts. Computer simulation can be useful in rectifying errors in the experimental parameters.

Introduction

Since it is known that all the diffuse scattering that occurs solely as the result of the nonrandomness in solid solutions is representable in terms of the Warren–Cowley short-range order parameters, it follows that only these parameters can be calculated from the observations of diffuse scattering. These parameters, called alphas, are related to the average composition within a given shell around a given central atom. Thus, they are expressible in terms of conditional probabilities. Having obtained a set of alphas, one normally wants to answer certain questions about the nature of the solution, questions that cannot be answered directly from the alphas but which could be addressed by use of a physical model. The problem of translating the alphas into a model that will reproduce them is a rather formidable task because of the large number of atoms that must be used to obtain the desired statistical accuracy.

Gehlen & Cohen (1965) first solved this problem by devising a computer program that rearranged the two kinds of atoms until the desired populations were obtained in the first three shells. The author devised a similar program (Williams, 1970) and over the years kept including more and more shells in the simulation without necessarily ever getting entirely satisfactory agreement between the data and the model. In particular, in the case of a copper-base aluminum alloy,

seven shells were not sufficient (Williams, 1974). Because of this continuing frustration of not being able to obtain the desired level of agreement, we decided to rewrite our program to model 18 shells in the hope that this would always be sufficient. Because of the large number of sites involved, we implemented the most efficient algorithm that we could devise. The possible small differences of the results produced by the new algorithm are masked by the effect of the inclusion of many more shells. The new program has been documented in a recent report (Williams, 1976).

As an extensive test of this new program, we have modeled most of the reasonably complete sets of data for face-centered cubic solutions. This was done not only to obtain a good base of experience with the new program, but also to determine the extent to which such simulation can identify and remove deficiencies in data sets. We have also included some information that characterizes the modeling process.

Model generation

The documentation report (Williams, 1976) gives the complete program along with the details of how it operates. Our comments here are limited to those required to make the present paper self-contained.

For a given model, one can calculate the number of 1–1 pairs for each shell that will agree with a prescribed set of alphas. (The minor species is identified as 1, the major as 0.) A pair is formed by a central 1 atom and a 1 atom in a shell. Further, at any stage of modeling one

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can determine the actual number of pairs. The difference between these two numbers for a given shell represents a component of our 18-component vector. The difference between a given model and a model that would exactly reproduce the data can be described in terms of the length for our 18-component vector.

A string of sites containing 0-1-0-1-... atoms is searched, and the resulting vector length if a given mixed pair were interchanged is calculated. The atoms are interchanged if this would shorten the vector length; otherwise the search is continued. The strategy used to decide which members of the string are saved as candidate pairs is as follows: Suppose that a new 1 atom is examined and the vector length is found to be greater than that for the best 1 atom previously examined in the string. In that case the previous 1 atom site is saved, not the new site. The same strategy applies to the 0 sites. The sites are picked in a random sequence constructed such that all sites of a given kind are examined before the sequence is repeated. The 18 shells in the design set contain 264 sites. Thus, each interchange requires the examination of not less than 528 sites. The actual number is typically 5000.

Each model contains 12 075 atoms, and eight independent runs are made. Error estimates for the model alphas are made from the deviation from the average. For those shells included in the model, this deviation will necessarily be very small for the case where the alphas can be matched. In any case the estimated error for the shells not included in the design set is typically 0.003.

It is interesting to examine the progress of the modeling as indicated by the length of the vector. Most of the present results are given in Fig. 1. The initial curves are rather similar and, in particular, the initial slopes appear to be almost identical. In three cases the magnitude of this slope increases at around 1000 interchanges, an effect most pronounced for the Al-Ag alloy.

On the basis of Fig. 1 the reader might deduce that the modeling could have been taken considerably

further for the Ni-Mo alloys. Actually, the modeling went just about as far as possible. There will always be a finite slope for these curves since each interchange must result in some decrease in vector length, even the last possible interchange. The approaching limit to the modeling process is most directly indicated by the scans required for each interchange becoming rather long (Williams, 1976).

We cannot demonstrate that no other method can produce models that will fit the observations better. But our method will, if carried to its absolute limit, produce a model in which no pairs remain which can be favorably interchanged (Williams, 1976). In this regard we have demonstrated that we can proceed a good deal further in modeling the Al-Ag results that when using the Gragg-modified Gehlen-Cohen method (Gragg & Cohen, 1971).

Error analysis for the alphas

The observed alphas, α_j , may be represented in terms of the true alphas, α_j^1 , by the expression:

$$\alpha_j = R(\alpha_j^1 + S_j), \quad (1)$$

where R is a scaling factor and the S_j are structural errors which depend upon the particular shell. The deviation of the scaling factor from the ideal value of unity arises primarily from uncertainties in the measurement of the absolute intensity of the X-ray beam. In particular, in the early work the average intensity was equated to the Laue monotonic intensity to provide standardization. More recently it has been established that there is extra intensity such that this means of standardization leads to the alphas too small in magnitude. We now have better means of standardization, but in any case an uncertainty of perhaps 5% is likely to be inherent in the standardization.

For a given set of alphas there is a critical scaling factor which will correspond to a limiting set of physically permissible alphas. From our modeling we can establish when a set of alphas has been scaled by some factor exceeding this critical value, for in that case it will be impossible to complete the modeling. We can make some rough estimates of how much the critical value has been exceeded by the magnitude of the differences in the alphas, but a precise value could be obtained only by rescaling the alphas until a set that could be modeled is obtained.

The presence of the S_j represents spurious structure in the intensity. It is instructive to consider the normal origin of this error. The standard way of obtaining the alphas consists of taking sufficient data, which can be so combined that one ends up with three components of intensity, which represent the alpha series, the first-order displacements and the quadratic intensity terms (which include the thermal diffuse scattering). Then one

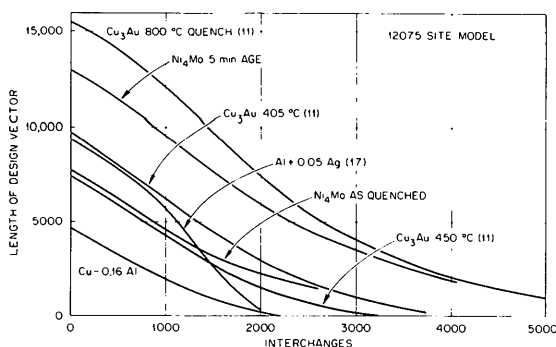


Fig. 1. Rate of model generation for selected data sets. For those cases where fewer than 18 shells were used the actual numbers are shown in parentheses.

carries out a Fourier transform of each component so as to obtain the desired parameters (Borie & Sparks, 1971). Any spurious data are now transformed and result in the S_i . This spurious intensity can show up in a number of ways, but a universal problem exists at the Bragg peaks. As one approaches the Bragg peaks, the data will always deteriorate, and no data can be obtained over the region where Bragg diffraction is occurring. Thus, one must always do some kind of smoothing and extrapolation in this region. Our belief is that this can generally be done satisfactorily for solid

solutions that show short-range order. In part this can be done because of the limited complexity of the diffuse scattering from such systems: the intensity is normally considered to vary smoothly over the extensive valleys and to peak locally, forming peaks and ridges. The problem that occurs is that in using large volumes of data with a computer program one may well not detect the presence of spurious features.

One cannot in general predict the probable sign of the S_i but one can, based on how the observations are made and the data reduced, make some predictions of

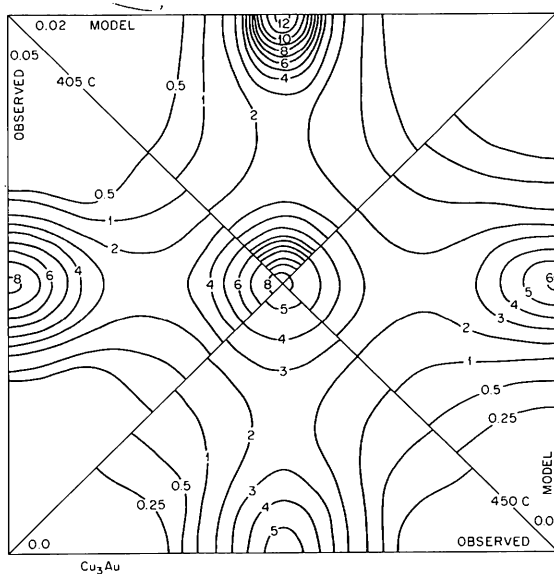


Fig. 2. Comparison of the observed and model short-range order intensity for Cu_3Au at 405 and 450°C.

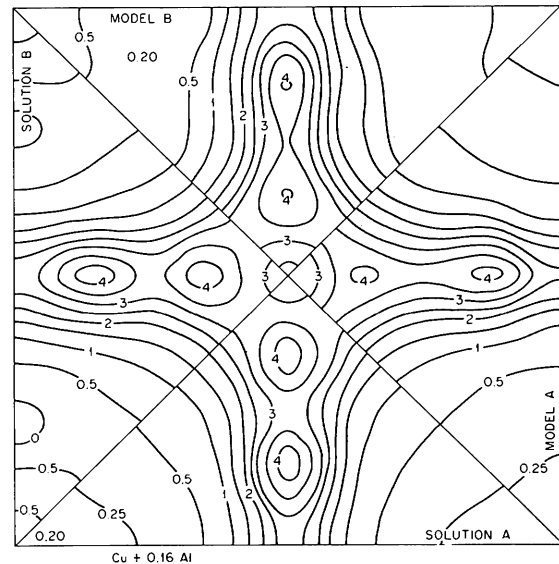


Fig. 4. Comparison of the observed and model short-range order for a Cu-16 at.% Al Alloy.

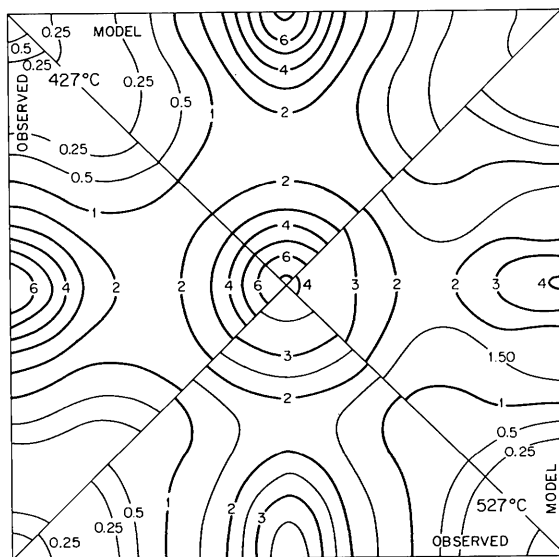


Fig. 3. Comparison of the observed and model short-range order intensity for CuAu at 425 and 527°C.

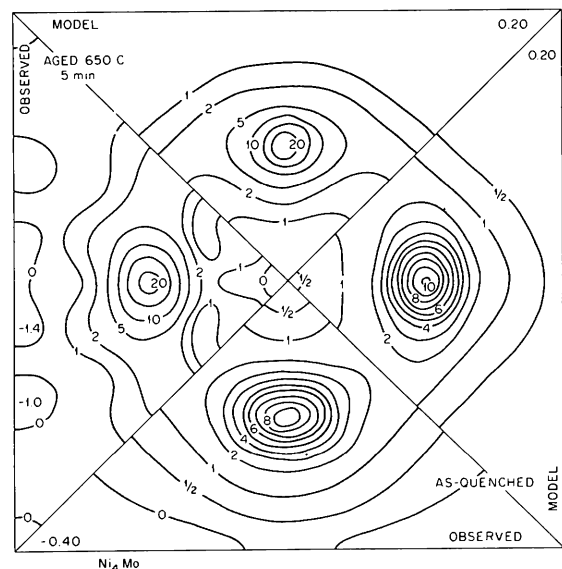


Fig. 5. Comparison of the observed and model short-range order intensity for Ni_4Mo as quenched and after a 5 min age at 650°C.

how the magnitude of the S_i will vary with the size (order) of the shells. We know that only a few low-order alphas may be reliably calculated from powder data. This means that the magnitudes of the S_i are rapidly increasing with shell order. For complete sets of

observations that contain only random errors, the magnitudes of S_i are independent of the shell order. If one constrains the solution such as to eliminate meaningless fine details, then the magnitude can decrease with order.

Table 1. Comparison of sets of alphas generated by simulation with the observed alphas for various metallic systems

The observed alphas are in the left column in each case; the units are $\alpha \times 1000$.

Shell	Cu ₃ Au (Moss, 1964)						CuAu (Metcalfe & Leake, 1975)					
	800°C quench		405°C		450°C		797°C quench		427°C		527°C	
110	-273	-242	-218	-209	-195	-191	-205	-203	-187	-184	-156	-156
200	450	437	286	289	215	217	444	442	230	230	180	180
211	-45	-45	-12	-10	3	4	-93	-94	-13	-13	-11	-11
220	240	245	122	124	77	78	289	289	109	109	38	38
310	-129	-125	-73	-72	-52	-51	-90	-91	-29	-30	-22	-22
222	149	148	69	69	28	29	218	218	30	30	11	11
321	-52	-52	-23	-23	-10	-10	-67	-67	-18	-18	-6	-6
400	92	113	67	68	36	36	198	197	37	36	38	38
330	-73	-74	-28	-28	-15	-15	-54	-53	-6	-6	0	0
411	19	23	4	4	7	7	-63	-63	-1	-2	17	17
420	108	106	47	47	15	15	153	153	22	22	-7	-7
233		-38		-17		-6	-42	-43	-1	-1	9	9
422		78		34		8	134	134	17	17	7	7
510		-45		-17		-5	-28	-36	-5	-6	-5	-13
431		-5		-4		1	-49	-49	-4	-4	5	5
521		-40		-12		-2	-28	-30	-4	-5	-5	-8
440		71		22		4	101	101	11	11	0	0
530		-37		-12		-5	-23	-23	2	0	1	-2
433		-9		-4		0	-35	-36	4	4	-6	-6
600		40		14		1	97	94	6	11	12	11
244		47		17		4	97	97		-1		-1
611		15		2		0	-51	-43		0		10
532		-24		-9		-4	22	-24		-4		-1
620		48		14		0	76	80		5		-2
541		-16		-3		1		-27		0		-1
622		43		12		1		73		4		1
631		7		2		1		-35		0		4
444		25		8		1		74		-8		4
550		-24		-8		-2		-13		-2		-2
710		-21		-4		1		-15		-3		-3
543		-10		-3		-1		-23		1		-1
640		35		8		1		60		1		0
633		1		2		2		-25		5		2
255		-13		-6		-2		-16		-1		1
721		-22		-4		0		-13		0		-1
642		26		6		1		58		1		2
730		-19		-5		0		-12		1		-1
732		-15		-5		-1		-12		-1		-1
651		-1		0		-1		-22		0		1
455		-5		-2		0		-15		0		0
800		26		5		-3		47		3		1
811		8		1		0		-24		-1		-1
644		15		3		1		47		-1		2
741		-12		-1		0		-12		0		1
820		24		3		0		41		1		-1
653		-3		1		0		-17		2		0
660		20		4		5		40		2		-1
822		21		4		1		38		0		1
743		-7		-1		-1		-12		-1		-1
750		-12		-3		-1		-8		-1		-1

Table 1 (cont.)

Shell	Cu-16 at.% Al (Williams, 1974)				Ni ₄ Mo (Chakravarti <i>et al.</i> , 1974)				Au ₆ Pd ₄		NiPd		Al ₉₅ Ag ₅	
	Solution A		Solution B		5 min age		As quenched		(Lin <i>et al.</i> , 1970)		(Lin & Spruiell, 1971)		(Gragg & Cohen, 1971)	
110	-164	-163	-161	-151	-243	-184	-204	-151	-126	-125	5	5	692	657
200	155	155	218	191	112	105	-10	18	61	61	184	184	483	493
211	41	41	54	50	170	144	114	104	29	29	-69	-69	426	432
220	30	30	-4	14	-186	-156	-72	-73	-33	-33	-12	-12	382	379
310	-61	-61	-61	-60	-103	-91	-64	-53	-25	-25	21	21	287	291
222	-34	-34	11	-10	-180	-193	-123	-124	-43	-43	-30	-30	262	266
321	4	4	5	4	81	77	34	31	13	13	-10	-10	237	231
400	53	53	-2	15	295	291	110	117	17	17	13	13	150	165
330	-18	-17	-21	-20	-45	-47	5	1	-15	-15	-5	-5	185	178
411	23	23	19	20	-99	-94	-46	-43	-2	-2	-6	-6	142	150
420	3	3	26	16	42	47	35	35	-1	-1	-9	-9	130	135
233	7	6	9	9	16	20	13	16	6	6	-5	-5	131	125
422	-15	-15	-29	-21	-36	-32	-14	-12	-9	-9	-3	-3	108	106
510	-22	-21	-28	-13	-47	-51	-16	-17	-2	6	7	7	56	76
431	7	7	5	5	-31	-36	-19	-21	4	4	-2	-2	90	93
521	1	-1	0	-5	49	47	15	14	3	7		4	45	62
440	-7	-7	-9	-3	91	100	29	30	-1	-1	-15	-15	54	63
530	-3	-4	2	-7	-31	-24	-9	-14	-2	0		-1	33	50
433	3	3	1	1	-7	-10	-11	-10	-2	-2	0	0	47	49
600	22	17	32	-12	-5	31	-25	-3	7	0		1	11	38
244	-7	-7	-10	-13	36	33	14	14	-2	-2	7	7	38	43
611	0	7	-3	3	45	44	27	22		-3		3	8	34
532	2	2		8	8	14	5	8		3		3	25	37
620	7	4		16	-39	-56	-30	-19		-1		-1	-1	31
541	3	2		3	-30	-38	-5	-7		-1		3		31
622	0	-3		-12	-78	-71	-22	-26		-4		0	-7	23
631	-2	1		-2	29	33	8	10		-2		1	-8	22
444	0	0		9	33	29	16	16		1	3	3		16
550	-1	2		-2	3	10	-4	-4		1		0		20
710	-3	-6		-1	-8	-25	16	-5		-1		2		21
543		0		0	-21	-17	-7	-6		-1		2		15
640		-1		-3	13	10	-5	4		0		-6		18
633		0		-3	29	19	14	7		0		1		12
255		2		3	21	24	-2	3		1		2		14
721		-1		-1	16	27	-3	4		0		2		17
642		-2		-1	-12	-8	-2	-6		0		3		12
730		-1		-3	-14	-20	-6	-3		-1		-1		15
732		1		4	10	0	2	4		-1		1		10
651		-1		-1	12	10	6	5		-1		2		12
455		-1		-3	-4	-3	0	-2		0		-2		-1
800		8		-4	48	75	17	16		3		-2		18
811		0		0		-32		-10		-3		-1		17
644		-1		1	10	6	-2	1		1		-1		0
741		-1		2	-17	-8	0	-3		0		0		11
820		3		4		17		8		2		-1		16
653		0		0	12	3	7	4		-1		1		2
660		0		0	-45	-25	-5	-6		-1		-4		9
822		0		-3		-3		1		1		0		11
743		0		1	-22	-4	-3	-3		0		2		3
750		2		-1	0	-4	-1	-3		0		-1		10

Results

We have examined 13 sets of data, and all data sets, including the model results, are listed in Table 1. Further, the intensities from the observed alphas and those from the models are compared in Figs. 2 through 6 for most data sets. The full 18-shell design set was

used if all these shells were included in the measurements.

The first three sets consist of measurements made by Moss (1964) on Cu₃Au on a quenched sample and at 405 and 450°C. The lower temperature is 15°C above the critical temperature for ordering. The second series of measurements consists of sets of observations

on CuAu by Metcalfe & Leake (1975), which are very similar to above measurements on Cu_3Au . The intensity maps for Cu_3Au and CuAu are compared in Figs. 2 and 3 respectively. In both cases, the quenched sample showed the greatest degree of order but did not appear to exhibit any new or unusual feature, and thus the intensity maps have not been included.

The parameters for the Cu–Al system were obtained (Williams, 1974) from a multiple-regression solution of the measurements by Borie & Sparks (1964). Solution *B* is defective in that the diffuse intensity becomes negative in certain regions not covered by the measurements. In solution *A* this defect is eliminated by the requirement that the diffuse intensity vary slowly around the Bragg peaks. The intensity map is given in Fig. 4.

The data for the Ni_4Mo are from the recent paper by Chakravarti, Starke, Sparks & Williams (1974), while the data for Au_6Pd_4 and NiPd are from the studies by Lin, Spruiell & Williams (1970) and Lin & Spruiell (1971). The intensity map is given in Fig. 6.

The data for the Al–Ag alloy are from the study by Gragg & Cohen (1971). As the intensity maps for the observations and the model consist primarily of strong maxima at the Bragg position, these maps have not been included.

Discussion

Strictly speaking, intensity maps and sets of alphas contain the same information, but it is rather easier to calculate the intensity from the alphas than *vice versa*. However, one is much more likely to detect questionable features in the intensity maps than in the sets of

alphas; in particular, the physically inadmissible negative regions are immediately recognized. Thus we emphasize here the comparisons between the intensity maps in contrast to earlier work in which only the alphas were compared.

There are four ways in which modeling results can constructively interact with sets of observations.

(1) The original set of alphas may have been terminated such that the intensity is not adequately represented. Modeling can extend the set.

(2) The set of alphas may be scaled so large as to be physically impossible. The presence of such a condition is immediately indicated from the modeling, and the magnitude of the supercritical scaling is assessable. A precise lower value can be obtained from rescaling the alphas until the model can be completed. The linear programming used by Gragg (1970) also addresses this problem, but we do not presently know the relative merits of the two approaches.

(3) Since the intensity from a model will not be negative, apart from termination effects, the model alphas will be superior to a set of observed alphas that leads to extensive negative regions. However, this improved set of alphas would not normally be superior to those obtained from retransforming the observed intensity after removing the negative regions.

(4) We will show that modeling identifies spurious features through their further enhancement.

We now examine the various sets of data to see how they fit into the above outline.

The Cu_3Au and CuAu data

Moss (1964) realized that his set of alphas was insufficient to fully describe the intensity, and the modeling has provided reasonably full sets, except for the quenched sample where still higher terms are of some importance. Further, we find that in no case can the modeling be completed, although we come very close for the 450°C data. From this it is clear that the alphas are large by a factor estimated to be 1.05. In this connection it is interesting to note that Moss originally undertook this investigation because he realized that equating the average diffuse intensity to the Laue monotonic intensity was questionable because of the extra intensity normally present. His were some of the first results using the scattering from polystyrene for standardization. His alphas were roughly 30% higher than those obtained by Cowley (1950) using Laue standardization. We can find no evidence for questionable structural features in these intensity maps and conclude that the structural errors are very small. Moss chose to have the diffuse intensity go smoothly to zero at the Bragg positions. To our knowledge, no one has demonstrated that a different behavior is more correct.

The ideal structure of ordered CuAu is tetragonal, with the same set of alphas as Cu_3Au provided that

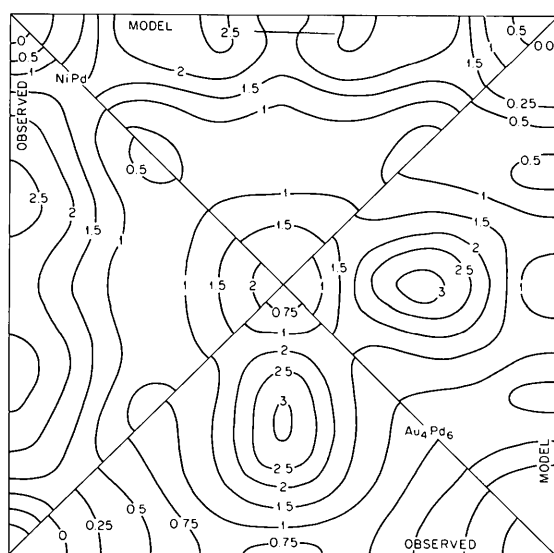


Fig. 6. Comparison of the observed and model short-range order intensity for NiPd and Au_4Pd_6 .

c/a is unity. Thus, one expects considerable similarity between these results by Metcalfe & Leake (1975) and those just discussed, and this similarity is indeed shown both by the alphas and by the intensity maps. There is a slight problem in that the intensity maps shown in the paper were not folded and averaged to represent fully the symmetry of the alpha series. This is of no consequence as far as the values of the alphas are concerned, but it does mean that our intensity maps will not precisely match theirs. We were able to match their alphas very closely with our models, and thus clearly their alphas are physically possible, neither being too large nor having negative intensity regions. Their alphas were slightly truncated, primarily for the quenched sample, and our results provide a reasonable extension. Further, we were able to find no questionable feature in the intensity maps for the quenched and the 470°C sample and conclude that for these cases the structural errors are quite small. We find a curious feature in the high-temperature data along the H_1 axis in that the intensity varies linearly for the sides of the peak, rather than forming the usual bell-shaped curve. It is precisely this feature that is markedly enhanced in the model, an observation in support of effect (4) above.

Cu-16 at.% Al

In solution *B*, the behavior of the diffuse intensity was unconstrained at the Bragg peaks and outside the two planes where the observations were made. This permitted a minor ripple near the Bragg peak but more importantly, the intensity took on a large negative value, -1.84 , at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. A second solution was obtained in which the diffuse intensity was constrained to vary slowly around the Bragg peaks to eliminate the negative intensity. We had previously shown that a six-shell simulation of solution *B* was entirely unsatisfactory (Williams, 1974) whereas here the present 18-shell simulation is considerably more acceptable. This is demonstrated both by Fig. 4 and by Table 1, where the model alphas almost invariably fall between the values for solution *B* and solution *A*. Previously we had found that a seven-shell simulation of solution *A* provided a single maximum rather than the split along the ridge, while the present 18-shell simulation represents the intensity very well, the only difference being that the ridge is slightly narrower.

Ni₄Mo

In the case of the quenched sample, we were unable to match the alphas too closely. This is shown in Table 1 and also by the vector length, Fig. 1. Part of the problem lies in the negative intensity at the Bragg position, but this would appear to be a minor problem; the larger effect is that the scaling factor has exceeded the critical value by an estimated 10%. The structural error in these data appears to be small. In

the case of the aged data a scaling error is still present but we also have more serious negative regions accompanying a more significant structural error. Why one set of data appears to be rather superior to the other is not presently known, but in any case, the simulation has presumably produced an improved set of alphas for the aged sample.

Au₄Pd₆ and NiPd

In the case of the Au₄Pd₆ data there is the problem that the given set of alphas does not fully reproduce the observed intensity. The original data exhibited a double peak similarly to the Cu-Al system rather than the single peak shown in Fig. 6. This may be entirely due to termination effects, but it is seen that there is also a curious dip in the intensity at 1,0,0, which surely cannot be due solely to termination effects. It is this later feature that is strongly enhanced by the model. We are forced to conclude that these data contain a significant structural error.

The results for the NiPd alloy are very interesting in that they are distinctly different from any of the previous results, all of which had some elements of similarity. There is nothing in these results that one can suggest as being suspect, although our unfamiliarity with such structures reduces the sensitivity in this case. We do find that some of the features of the model, primarily the intensity distribution around 1,0,0, are questionable and conclude that these arise from unrecognized defects in the observations. That the problem occurs at the same position as for the Au-Pd alloy suggests that a common problem exists in the two sets of data.

The Al-Ag precipitation system

These data are included primarily as a common point between our modeling program and that due to Gehlen & Cohen (1965) as modified by Gragg (1970). The significant point in this regard is that we were able to carry the modeling considerably further in spite of the fact that we were fitting 17 shells rather than their four. To understand why this should be, would require a careful look into the interworkings of their program.

It has been well established that the diffuse scattering that occurs for the initial stage of precipitation, the GP zones, consists of halos around the Bragg peaks. These arise from a more or less random arrangement of spherical particles, which contain roughly 60% Ag. During competitive growth we expect the morphology to remain fixed since the strain energy in the system is very small. This means that the character of the halos would remain constant although the diameters would be inversely related to the particles size (or separation). For the data of Gragg & Cohen (1971) to be consistent with this picture requires that their series must be severely truncated since the intensity calculated from

their alphas has strong maxima at the Bragg peaks rather than the required minima. Our alphas from the model may also be truncated, but the structure of the model is highly suspect, for instead of the spherical Ag-rich regions the structure consists of irregular sheets or strings of Ag atoms, a structure that is surely incorrect. Our model structure is also distinctly different from that produced by Gragg & Cohen (1971), but we are unable to decide how much this results from the increased number of shells, and how much from the basic differences in the two programs. Our model gives strongly enhanced maxima at the Bragg peaks, again in agreement with item (4) above.

Excluded data sets

Recently, Ohshima, Watanabe & Harada (1976) have given a set of alphas for a Cu-29.8 at.% Pd alloy. The short-range order observed in this system is intermediate between Cu₃Au and Cu-16 at.% Al systems as given here. No modeling has yet been run on these data.

Bardhan & Cohen (1976) have recently published a detailed set of alphas for Cu₃Au as a function of temperature, starting immediately above the critical temperature. These data show complex temperature dependence. Modeling these alphas was rather unsuccessful as indicated, for example, by the complexity of the resulting intensity maps. To further investigate the quality of these parameters we reanalyzed one set of the data very kindly supplied by Cohen, using a least-squares fitting method (Williams, 1972) and found that we were able to fit the observations much better than did their published parameters, indicating clearly that there are errors in their data reduction program. The precise nature of the difficulty is unknown but appears to be associated with the Bragg peaks, as if resulting from the missing observations in this region. The Al-Ag data were processed by the sample program and appear to exhibit similar deficiencies.

General discussion

It would appear that the magnitudes of the scaling errors in these collective data are rather small. This is a subjective evaluation, but it is of some comfort that only in roughly one-third of the cases are the alphas demonstrably too large in magnitude and then only by 5 to 10%. What is more disturbing is the frequency of unnecessarily large structural errors. What has happened is that as more extensive sets of data are taken such that more sophisticated data reduction methods can be used, utilization of the computer for data processing has increased. Under these circumstances it is all too easy for artifacts to remain in the maps that are transformed. We have clearly shown that such artifacts go undetected in the alphas.

That modeling eliminates negative intensities and also demonstrates the existence of alphas that are too large in magnitude are results that we consider generally known in the field. Our only claim is that we have more extensively demonstrated these effects and have, in some cases, offered sets of alphas that should be more reliable. The case for modeling is a good deal less optimistic than originally believed by Gehlen & Cohen (1965) – that the first three alphas sufficiently define a structure. It appears that 18 shells are sufficient, but unquestionably there are cases where fewer would be adequate.

If our conclusion that modeling identifies spurious features in the intensity map through their further enhancement stands up to more extensive testing, then this could be a most useful result. Our understanding of how this effect comes about is as follows. Let us suppose that we have a set of data like Moss's (1964) Cu₃Au data, which is characterized by domains having an average size, shape, and degree of internal perfection. Now we introduce an artifact into the intensity map, which results in a number of higher-order alphas changing substantially in magnitude. Now, if some of these perturbed alphas are in the design set this will cause some kind of longer-range structure to be built up. This might be a phasing between neighboring domains or the introduction of some peculiar shape; the domains might grow arms, for example. In any case this long-range effect also persists in the higher shells outside the design set, which is the origin of the enhanced intensity. This effect cannot operate, or operates to a reduced extent, in the case of negative intensities or when the alphas are too large, for in these cases the model alphas are physically restrained.

There have been recurring statements in the literature which describe the structure of concentrated alloys showing short-range order as consisting of small, highly ordered regions dispersed in a disordered matrix, the most recent due to Thomas & Sinclair (1977) in a discussion of a paper by Chevalier & Stobbs (1976) on Ni₄Mo. The maximum amount of disordered material which is present can be severely restricted by the large magnitude of the alpha for the first shell which can be easily shown as follows. If X is the fraction of the material which is ordered then the alpha for the first shell is given as

$$\alpha = X\alpha_0 \quad (2)$$

by taking the alpha for the disordered material as zero, and where α_0 is for perfect order. We take the surface atoms of the ordered regions to be half in the disordered matrix such that a surface term is not required. The ordered fractions corresponding to the largest alphas in Table 1 are 0.82 for Cu₃Au, 0.62 for CuAu, 0.97 for Ni₄Mo and 0.86 for Cu-Al. We have already indicated that the value for Ni₄Mo is too large, the correct value being nearer 0.90. These values would be further increased if the order were less than perfect and,

for these high fractions, there must be some antiphase material which must further reduce the disordered material. Thus, the X-ray results clearly show that the amount of disordered material is, at most, only a minor fraction, a conclusion we had already reached for the Cu-Al data (Williams, 1974).

Summary and conclusions

We have developed a computer program that simulates solid solutions by matching the atom populations in 18 shells. This program has been used on 13 sets of data from f.c.c. solid solutions. Our principal conclusions follow.

The use of 18 shells appears to be adequate for this purpose; previously it had been demonstrated that seven were not necessarily sufficient.

Two investigations have been found in which the alphas are of too great a magnitude, an effect that probably arose from uncertainties in beam standardization. The values are estimated to be high by at least 5%.

Several sets of alphas corresponded to negative intensities in certain locations. The model alphas, in part, correct these data sets.

Several data sets were incomplete in that they were truncated. The present work extended all sets to a full 50 shells.

We have made a very interesting observation that the defects in the intensity maps can be identified by a further enhancement from modeling.

With one exception we find all these sets of alphas to be of reasonable quality. A problem not generally recognized is that frequently the measurements contain spurious details, which should have been rectified before the Fourier transform. The use of computer processing of the data has contributed to this problem.

These results clearly show that intensity maps provide a more reliable indication of data quality than

do the alphas. Further, such maps can make comparisons easier.

The magnitude of the alpha for the first shell indicates that the amount of disordered material in many of these structures must be minor.

References

- BARDHAN, P. & COHEN, J. B. (1976). *Acta Cryst.* **A32**, 597-614.
- BORIE, B. S. & SPARKS, C. J. (1964). *Acta Cryst.* **17**, 827-835.
- BORIE, B. S. & SPARKS, C. J. (1971). *Acta Cryst.* **A27**, 198-201.
- CHAKRAVARTI, B., STARKE, E. A., SPARKS, C. J. & WILLIAMS, R. O. (1974). *J. Phys. Chem. Solids*, **35**, 1317-1326.
- CHEVALIER, J.-P. A. A. & STOBBS, W. M. (1976). *Acta Metall.* **24**, 535-542.
- COWLEY, J. M. (1950). *J. Appl. Phys.* **21**, 24-30.
- GEHLEN, P. C. & COHEN, J. B. (1965). *Phys. Rev. A*, **139**, 844-855.
- GRAGG, J. E. (1970). Thesis, Northwestern Univ., Evanston, Ill, USA.
- GRAGG, J. E. & COHEN, J. B. (1971). *Acta Metall.* **19**, 507-519.
- LIN, W. & SPRUIELL, J. E. (1971). *Acta Metall.* **19**, 451-461.
- LIN, W., SPRUIELL, J. E. & WILLIAMS, R. O. (1970). *J. Appl. Cryst.* **3**, 297-305.
- METCALFE, E. & LEAKE, J. A. (1975). *Acta Metall.* **23**, 1135-1143.
- MOSS, C. S. (1964). *J. Appl. Phys.* **35**, 3547-3553.
- OHSHIMA, K., WATANABE, D. & HARADA, J. (1976). *Acta Cryst.* **A32**, 883-892.
- THOMAS, G. & SINCLAIR, R. (1977). *Acta Metall.* **25**, 231-234.
- WILLIAMS, R. O. (1970). Report ORNL-TM-2866. Oak Ridge National Laboratory, Tennessee.
- WILLIAMS, R. O. (1972). Report ORNL-4828. Oak Ridge National Laboratory, Tennessee.
- WILLIAMS, R. O. (1974). *Metall. Trans.* **5**, 1843-1850.
- WILLIAMS, R. O. (1976). Report ORNL-5140. Oak Ridge National Laboratory, Tennessee.