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BNL 6671

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A Re-analysis of Short-Range Order in Cu_3Au *

by

C. B. Walker

Institute for the Study of Metals, University of Chicago, Chicago 37, Ill.

and

D. T. Keating

Brookhaven National Laboratory, Upton, New York

ABSTRACT

Cowley's measurements of the short-range order parameters, α_i , in Cu_3Au at $T = 405^\circ\text{C}$ have been re-evaluated taking into account the effects of thermal vibrations and static displacements due to differing atomic sizes. The separate corrections for the thermal vibrations and the first-neighbor atomic size factor are found to be quite large, demonstrating their importance in the usual experiments. When combined, the corrections in this case largely cancel, and only the values of α_1 and α_3 are appreciably changed. The corrected values are: $\alpha_1 = -.113$, $\alpha_2 = +.185$, $\alpha_3 = -.009$, $\alpha_4 = +.082$, $\alpha_5 = -.058$.

* Research supported by the U. S. Atomic Energy Commission and by the U. S. Army Research Office (Durham).

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

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Introduction

In 1950 Cowley¹ published an X-ray diffuse scattering study of short-range order in Cu_3Au that has been probably the most significant single experimental study in this field. Since that time the theory of the diffuse scattering due to local order in binary alloys has been extended to include the effects of several additional factors: local static displacements due to differing atomic sizes;² long range static displacements due to differing atomic sizes;³ and, most recently, thermal vibrations.^{4,5} The inclusion of these factors modifies the diffuse scattering theory appreciably, so we decided to re-evaluate Cowley's results for one temperature in terms of this more complete theory, both to illustrate the effects of the various factors and to obtain a better set of values for the short-range order parameters in Cu_3Au .

In the original theory the atoms of the alloy are assumed to be located precisely on the sites of the average lattice, and the intensity of the short-range order scattering, in Laue monotonic units, is given by

$$I_{\text{SRO}} = \sum_i \alpha(r_i) \cos(\bar{K} \cdot \bar{r}_i), \quad (1)$$

where the $\alpha(r_i)$ are the short-range order parameters; \bar{K} is the difference between the wave-vectors of the scattered and incident radiation; \bar{r}_i is the vector between the origin site and site i ; and the sum extends over all sites. When the effects of thermal vibrations and differing atomic sizes are included, the expression for the short-range order scattering is modified and additional terms representing size effect scattering appear. The intensity of this combined diffuse scattering, in Laue monotonic units, is given approximately by

$$I_D = \sum_i a(r_i) e^{-C_i |K|^2} \cos(\vec{K} \cdot \vec{r}_i) - \sum_{i \neq 0} b(r_i) e^{-C_i |K|^2} (\vec{K} \cdot \vec{r}_i) \sin(\vec{K} \cdot \vec{r}_i),$$

(2)

where the $\beta(r_i)$ are local size effect parameters. The exponential attenuation factors arise from both thermal vibrations and static strains; the exponent can be written $C_i |K|^2 = 2M\gamma(r_i) + 2M'\gamma'(r_i)$, where $2M$ is the usual Debye-Waller factor, $2M'$ is a similar static strain factor, and $\gamma(r_i)$ and $\gamma'(r_i)$ are displacement correlation factors that vary from zero at $r = 0$ to unity for large r . There is an additional scattering due to static strains, the so-called Huang scattering, that concentrates near crystalline reflections, but for our present purposes that term can be neglected.

Cowley's procedure was the following: The diffuse scattering from a single crystal of Cu_3Au was measured in arbitrary units throughout the segment of the unit cell, ABCDEF, in reciprocal space shown in Fig. 1. These measured intensities were corrected for Compton and thermal diffuse scattering and for various angular factors, and the resulting corrected scattering, I_M , was considered to be the short-range order scattering; that is

$$c I_M = I_{SRO}, \quad (3)$$

where c is a constant to convert the arbitrary units of the measurements to Laue monotonic units. Next this corrected scattering was extended using the symmetry of the reciprocal lattice to give a symmetrized corrected scattering, I_{MS} , throughout a unit cell of reciprocal space, and then Fourier transforms were

made of this symmetrized corrected scattering:

$$T(\bar{r}_j) = \frac{1}{V_{\bar{K}}} \iiint_{V_{\bar{K}}} I_{MS} \cos(\bar{K} \cdot \bar{r}_j) d\bar{K} \quad (4)$$

where $\frac{V}{\bar{K}}$ is the volume of the reciprocal space unit cell. From Eq. (1) and (3),

$$cT(\bar{r}_j) = \alpha(r_j); \quad (5)$$

and since $\alpha(0) \equiv 1$, $c = 1/T(0)$, and the values of the short-range order parameters were completely determined.

In terms of the more complete theory, Cowley's corrected scattering, I_M , must now be regarded as the combined short-range order and size-effect scattering; that is,

$$cI_M = I_D \quad (6)$$

Our problem is to evaluate Eq. (4) in terms of Eq. (2) and (6) in order to find out what the experimental Fourier transforms, $T(r_j)$, actually represent.

Analysis

Let:

$$\begin{aligned} \bar{r}_j &= \frac{1}{2} (x_j \bar{a}_1 + y_j \bar{a}_2 + z_j \bar{a}_3), \\ \bar{K} &= 2\pi (h_1 \bar{b}_1 + h_2 \bar{b}_2 + h_3 \bar{b}_3), \\ C_j |K|^2 &= R_j (h_1^2 + h_2^2 + h_3^2), \end{aligned}$$

where the \bar{a}_i are the real lattice vectors; the \bar{b}_i are the reciprocal lattice

vectors; x_j , y_j , and z_j are integers defining the position of site j ; and the h_i are continuous variables in reciprocal space. Using the symmetry of the face-centered cubic real lattice of Cu_3Au , Eq. (2) can be written

$$I_D = \sum_l a_l e^{-R_l(h_1^2+h_2^2+h_3^2)} \cos(\pi x_l h_1) \cdot \cos(\pi y_l h_2) \cdot \cos(\pi z_l h_3) - \pi \sum_{l \neq 0} \beta_l e^{-R_l(h_1^2+h_2^2+h_3^2)} \left\{ \begin{array}{l} x_l h_1 \sin(\pi x_l h_1) \cdot \cos(\pi y_l h_2) \cdot \cos(\pi z_l h_3) \\ + y_l h_2 \cos(\pi x_l h_1) \cdot \sin(\pi y_l h_2) \cdot \cos(\pi z_l h_3) \\ + z_l h_3 \cos(\pi x_l h_1) \cdot \cos(\pi y_l h_2) \cdot \sin(\pi z_l h_3) \end{array} \right\}, \quad (7)$$

where we have adopted the shorter notation, $\alpha(r_i) = \alpha_i$ etc. Using the symmetry of the body-centered reciprocal space of Cu_3Au , Eq. (4) reduces to

$$T(x_j, y_j, z_j) = 2 \iiint_V I_M \cos(\pi x_j h_1) [\cos(\pi y_j h_2) \cdot \cos(\pi z_j h_3) + \cos(\pi z_j h_2) \cdot \cos(\pi y_j h_3)] dh_1 dh_2 dh_3, \quad (8)$$

where the integral extends only over the volume, V , of the segment of the unit cell shown in Fig. 1.

Eq. (8) is now to be evaluated using Eq. (6) and (7). These transforms will take the general form of a linear combination of short-range order and size-effect parameters,

$$cT(x_j, y_j, z_j) = \sum_i A_{ij} a_i + \sum_{i \neq 0} B_{ij} \beta_i.$$

where the coefficients A_{ij} and B_{ij} depend on the perturbing thermal vibrations

and long-range atomic size effects expressed by the R_i . If the R_i are zero (i.e., no perturbing effects) $A_{ii} = 1$ and all A_{ij} ($i \neq j$) are zero; as the R_i increase, the A_{ii} decrease and the off-diagonal A_{ij} 's increase. The B_{ij} cannot be described in as simple a fashion⁶, but their dependence on the R_i is more or less the same: with increasing R_i those B_{ij} that are non zero for $R_i = 0$ tend to decrease while the other B_{ij} increase.

We have carried through a detailed evaluation of the various transforms using data appropriate to Cu_3Au at 405°C . For simplicity the unknown short-range order parameters were assumed to be negligible for sites beyond fifth neighbors. The value for the first neighbor size-effect parameter, $\beta_1 = +.015$, was taken from Warren, Averbach, and Roberts;² all other β_i were assumed to be negligible. The contributions of the thermal vibrations, $R_i(T)$, to the R_i were calculated from Quimby's elastic constant Debye temperature,⁷ $\Theta = 238^\circ\text{K}$ (viz, $2B = 2.66\text{\AA}^2$), and the contributions of the static strains $R_i(S)$ were calculated from Borie's X-ray measurements³ (viz, $2B' = 0.43\text{\AA}^2$); the values of these quantities for the various neighboring sites are given in Table I. The computation of the coefficients in the transforms was quite tedious and will not be described here; the values for the dominant terms, A_{ii} and B_{ii} , are accurate to 0.2%, while the small off-diagonal A_{ij} 's are accurate to 2%.

A first result was the demonstration that the transforms should not be invariant under permutation of the indices x, y, z , just as was observed experimentally by Cowley. Such asymmetry could be expected from the form of Eq. (8), but the magnitude in some cases was surprisingly large. For example,

$$cT(110) = .807\alpha_1 + .021\alpha_2 + .026\alpha_3 + .003\alpha_4 - .003\alpha_5 - .613\beta_1$$

$$cT(011) = .817\alpha_1 + .007\alpha_2 + .053\alpha_3 + .004\alpha_4 - .020\alpha_5 - 3.882\beta_1 .$$

Anticipating the final results, these equations lead to the ratio,

$$T(110) : T(011) = -.096 : -.148 = .649 .$$

This difference is due almost entirely to the difference in the size-effect terms.

In order to minimize the errors from the observed asymmetry, Cowley averaged the transforms over the permutations of their indices. Carrying out this same averaging, we find finally that the mean experimental Fourier transforms actually represent the following:

$$\begin{aligned} c\langle T(000) \rangle &= 1 + .106\alpha_1 - .002\alpha_2 - .074\alpha_3 - .003\alpha_4 + .025\alpha_5 - 16.106\beta_1 = 1.000c \\ c\langle T(110) \rangle &= .810\alpha_1 + .016\alpha_2 + .035\alpha_3 + .003\alpha_4 - .009\alpha_5 - 1.703\beta_1 = -.152c \\ c\langle T(200) \rangle &= .028\alpha_1 + .746\alpha_2 + .021\alpha_3 - .001\alpha_4 + .055\alpha_5 + .464\beta_1 = +.186c \\ c\langle T(211) \rangle &= .015\alpha_1 + .005\alpha_2 + .765\alpha_3 + .019\alpha_4 + .008\alpha_5 + .896\beta_1 = +.009c \\ c\langle T(220) \rangle &= .003\alpha_1 - .001\alpha_2 + .038\alpha_3 + .740\alpha_4 + .016\alpha_5 + .791\beta_1 = +.095c \\ c\langle T(310) \rangle &= -.004\alpha_1 + .013\alpha_2 + .008\alpha_3 + .008\alpha_4 + .758\alpha_5 + .052\beta_1 = -.053c , \end{aligned}$$

(9)

where the mean transforms have been equated to the reported values for the short-range order parameter at 405°C. This set of simultaneous equations can now be solved, using the known value of β_1 , to yield the corrected values for the

short-range order parameters in Cu_3Au at 405°C listed in column (4) of Table II.

For comparison, if the thermal vibration and long-range static displacement effects are ignored and only first-neighbor atomic size effects are included, the corresponding relations for the mean transforms are:

$$\begin{aligned}c\langle T(000) \rangle &= 1 - 20.211 \beta_1 = 1.000 c \\c\langle T(110) \rangle &= \alpha_1 - 1.968 \beta_1 = -.152 c \\c\langle T(200) \rangle &= \alpha_2 + .600 \beta_1 = +.186 c \\c\langle T(211) \rangle &= \alpha_3 + 1.100 \beta_1 = +.009 c \\c\langle T(220) \rangle &= \alpha_4 + .983 \beta_1 = +.095 c \\c\langle T(310) \rangle &= \alpha_5 + .037 \beta_1 = -.053 c .\end{aligned}\tag{10}$$

The values for the short-range order parameters obtained from these equations are listed in column (3) of Table II.

Discussion

An examination of the results given in Table II shows that both the first neighbor atomic size displacements and the thermal vibrations produced appreciable effects in the analysis of Cowley's diffuse scattering data. The primary effect of the first neighbor atomic size factor was to change the normalization transform, $T(000)$, by approximately 30%, producing a comparable change in the values of all the short-range order parameters. This large effect is a consequence of the choice of the particular volume segment, V , and could be expected to be quite different (even opposite in sign) for other volume segments; for example, the effect would be quite small if the volume investigated were a complete unit cell. A secondary effect of the first-neighbor atomic size factor was to introduce smaller terms into each $\langle T(xyz) \rangle$, which, in the case

of the small α_3 , led to a reversal of the sign. The effect of the thermal vibrations (and the much smaller long-range atomic size factor) was to alter the value of the short-range order parameters by approximately 25%, this change being opposite to that produced by the first neighbor atomic size factor. The effects here then tend to cancel, with the first neighbor atomic size effect being slightly more important. When the factors are combined, the corrected value for α_1 is 25% smaller in magnitude than that originally reported, α_3 is reversed in sign but still small, and the other three parameters are changed by only small amounts.

These corrected values for the short-range order parameter are believed to be a better set of values for Cu_3Au at 405°C than those given by Cowley. The limits of error to these values are quite large, primarily because of the uncertainty in the value of the parameter β_1 , which controls the large size-effect corrections. Estimating that the value of β_1 is only accurate to $\pm 50\%$, we find that the corresponding ranges for the systematic error in α_1 , α_2 , α_3 , α_4 , and α_5 are respectively approximately $\pm 35\%$, 20% , 100% , 25% , and 20% . The errors due to the various approximations in this analysis should all be negligible compared to this.

The method that we have used here to interpret Fourier transforms will generally involve rather tedious calculations, and we suggest that a least-squares procedure is probably a more advantageous technique for analyzing diffuse scattering data. Regardless of the method used, this re-analysis has demonstrated that it is quite important to correct for the perturbing temperature and size-effect factors in a typical short-range order scattering experiment.

Table I

Attenuation Coefficients* for Cu_3Au at 405°C

i	$x_i y_i z_i$	$R_i(T)$	$R_i(S)$	R_i
0	000	.0000	.0000	.0000
1	110	.0343	.0020	.0363
2	200	.0404	.0037	.0441
3	211	.0404	.0045	.0448
4	220	.0404	.0049	.0452
5	310	.0409	.0052	.0461

* For large i , $R_i(T) = .0472$, $R_i(S) = .0075$, and $R_i = .0547$

Table II

Short-Range Order Parameters for Cu_3Au

(1) For perfect order. (2) As given by Cowley for $T = 405^\circ\text{C}$. (3) Corrected only for first-neighbor atomic size effects. (4) Corrected for first neighbor atomic-size effects, long range size effects, and thermal vibration effects.

	α_i			
i	(1)	(2)	(3)	(4)
1	-1/3	-.152	-.076	-.113
2	1	+.186	+.121	+.185
3	-1/3	+.009	-.010	-.009
4	1	+.095	+.052	+.082
5	-1/3	-.053	-.038	-.058

Figure Captions

Fig. (1) The prism, $V = ABCDEF$, throughout which Cowley's diffuse measurements were made.

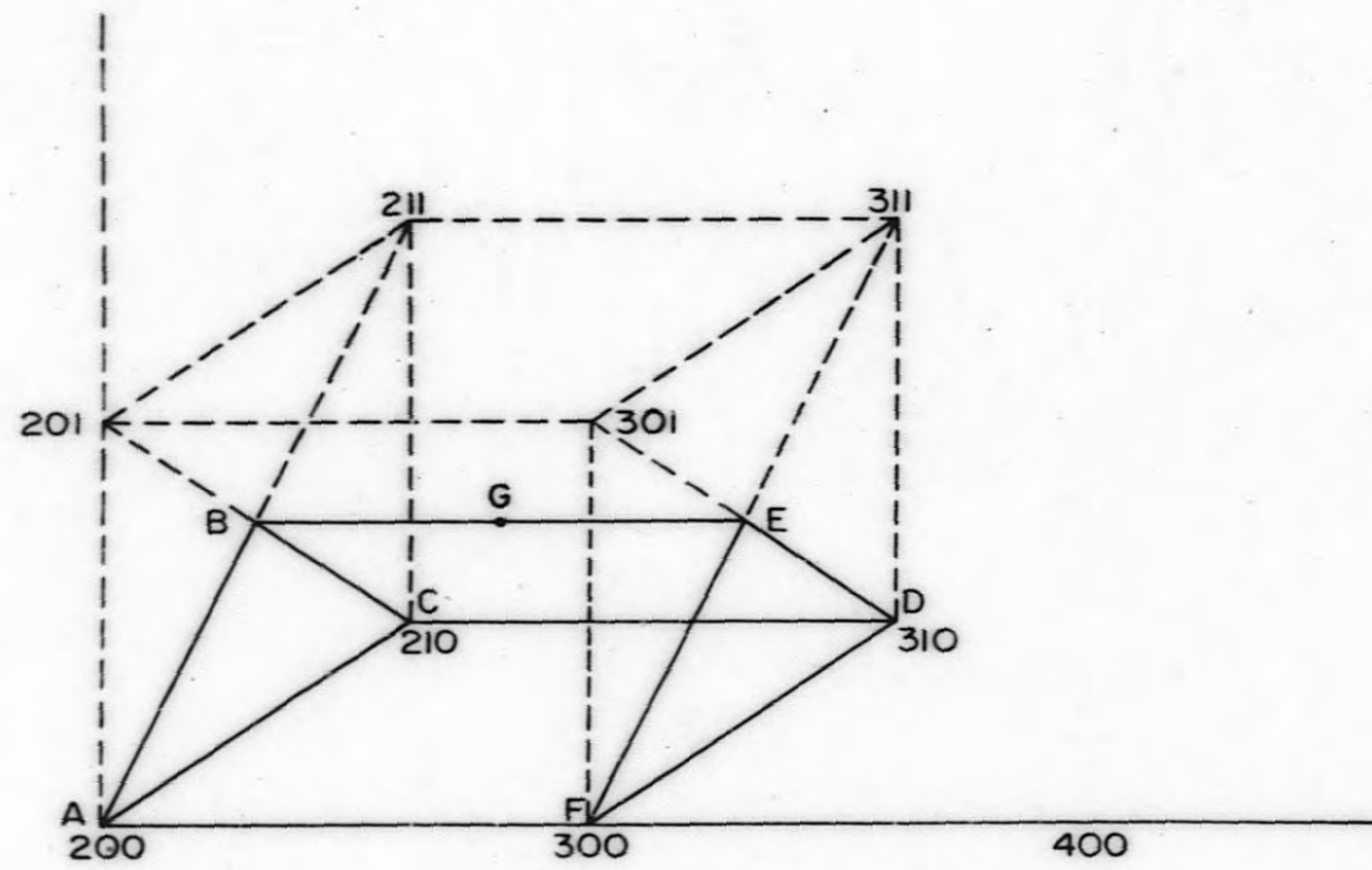


Fig 1

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