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# Determination of Long-Range Interaction Energies from the Scattering of X Rays by Disordered Alloys

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A method for determining the interparticle interaction energies in a disordered alloy from the corrected diffuse scattering intensities of x rays is presented. This method, which is based on the ordering theories, is applied to the problem of obtaining the first seven pair-interaction ratios in $Cu_3Au$ from the experimental data of Moss. Strong evidence for the presence of long-range pair interactions originating from the indirect screening interaction between ions is obtained for $Cu_3Au$, indicating the existence of a reasonably sharp Fermi surface in this alloy, at temperatures of the order of 700 °K.

## I. INTRODUCTION

One of the principal objectives in experimentally investigating short-range order in a binary alloy is to obtain information on the magnitude, sign, and range of the interparticle interaction energies in such a system. The current state of alloy theory suggests that a realistic comparison between empirical and theoretical values for these interactions is possible.

Clapp and Moss,[1-3] in a recent series of papers (Ref. 3, in particular), obtained indications of the existence of an oscillatory interaction in the Cu-Au system by an indirect method requiring diffuse scattering data from alloys with different compositions. We present a method which indicates an oscillatory interaction through experimental results from a single alloy system.

The pair-interaction model[1-4] assumes the energy of the binary alloy $AB$, with atom fractions $(m_A, m_B)$ to be decomposable into the sum of interactions $V_{ij}^{AA}$, $V_{ij}^{BB}$, $V_{ij}^{AB}$, and $V_{ij}^{BA}$, between pairs of atoms $(A, B)$ at sites $i$ and $j$ and a term independent of configuration at constant volume. The pair-interaction energy parameter is usually defined as

$$V_{ij} = \tfrac{1}{2}(V_{ij}^{AA} + V_{ij}^{BB} - 2V_{ij}^{AB}) . \quad (1.1)$$

This model for calculating the energy of a binary alloy should improve in reliability as the size difference between the $A$- and $B$-type atoms decreases, when the contributions of irreducible $n$-body $(n > 2)$ strain-energy terms will likewise diminish.[2,5]

For zero-size-effect binary alloys of nontransi-

tion metals in which the difference in the potentials of the two species is small, the expansion of the total energy to second order in perturbation theory is a good approximation. This expansion can readily be shown to be expressible in the form of the pair-interaction model.[4,6-8]

The method for obtaining information about the interaction energies depends on the representation of the ordering problem in the alloy, by the many-neighbor Ising model. Mathematical approximations to this model[1,2,9-12] (see also Sec. II) relate the corrected diffuse x-ray scattering $\alpha(\vec{k})$ to $V(\vec{k})$, the Fourier transform of the pair interaction. For $V(\vec{k})$ the expression

$$V(\vec{k}) = \sum_i V_{0i} e^{i\vec{k}\cdot\vec{r}_{oi}} \tag{1.2}$$

can be written, where $\vec{r}_{oi}$ is the lattice vector connecting site $i$ to the origin, $\vec{k}$ is $2\pi$ times the true reciprocal-space vector, and the sum is over all sites in the lattice (with $V_{oo} \equiv 0$).

The values of the pair-interaction ratios are determined more accurately than the absolute values (see Ref. 2 and also Sec. II). In this paper, the first seven pair-interaction ratios (single subscripts refer to shell numbers)

$$\frac{V_2}{V_1}, \frac{V_3}{V_1}, \frac{V_4}{V_1}, \frac{V_5}{V_1}, \frac{V_6}{V_1}, \frac{V_7}{V_1}, \frac{V_8}{V_1} \tag{1.3}$$

are determined for $Cu_3Au$, from the values of the Fourier coefficients of $\alpha(\vec{k})$;

$$\alpha_{0i} = \int \alpha(\vec{k}) e^{i\vec{k}\cdot\vec{r}_{oi}} d\vec{k} , \tag{1.4}$$

obtained by Moss[13] above the critical temperature.

The alloy $Cu_3Au$ has been chosen for initial investigation because the values of $\alpha_i$ obtained by Moss are believed to be the most accurate available and the requirements for the pair-interaction model appear to be well satisfied in this case.

## II. ORDERING THEORIES

The common ordering theories for predicting the diffuse scattering intensity from an alloy, which are approximate solutions to the Ising model, for example, the spherical model[10,11] and mean-field theory,[1,11,12] may be represented by the general form

$$\alpha(\vec{k}) = \frac{G_2(T)}{1 + G_1(T)\, V(\vec{k})} , \tag{2.1}$$

where $G_1$ and $G_2$ are essentially temperature-dependent factors and $G_2$ is chosen such that $\int \alpha(\vec{k})\, d\vec{k} = 1$. This form is found to be a very accurate solution for the special case of the nearest-neighbor equiatomic Ising model.[12] For the many-neighbor Ising model, Brout[11] has shown that the inclusion of all terms of $O(1/z)$ in the cluster expansion for $\alpha_{ij}$ also leads to a result of the form (2.1) (in fact, the same result as for the spherical model), where $z$ is a measure of the range of the interaction $V_{ij}$. Thus the form (2.1) should also be quite accurate for long-range interactions.

Following Clapp and Moss,[3] a critical temperature may be defined as the temperature at which the denominator in (2.1) first goes to zero from above for $\vec{k}$ at a point $\vec{k}_m$ for which $V(\vec{k}_m)$ is a global minimum in reciprocal space. Then $T_c$ is determined by

$$-1 = G_1(T_c) V(\vec{k}_m) , \tag{2.2}$$

and substituting this in (2.1) to obtain

$$\alpha(\vec{k}) = \frac{G_2(T)}{\{1 - [G_1(T)/G_1(T_c)][V(\vec{k})/V(\vec{k}_m)]\}}$$

$$= \frac{G_2(T)}{\{1 - [1/X(T)](T_c/T)[V(\vec{k})/V(\vec{k}_m)]\}} , \tag{2.3}$$

where

$$G_1(T_c)/G_1(T) = (T/T_c) X(T) . \tag{2.4}$$

The term in the second square brackets in (2.3) depends only on the ratios of the $V_i$, and $X(T)$ depends only on the particular approximation chosen, the temperature, and possibly the composition. In the mean-field approximation, $X(T) \equiv 1$ for $T \geq T_c$.

If the $T$ dependence of $X(T)$ is now considered, comparison of the mean-field or similar approximations with the Fisher and Burford result[12] and the Tahir-Kheli result[9] suggest that if $X(T)$ is taken in one of these approximations it will be in significant error. This may be expected to lead to considerable errors in the interaction ratios determined from $\alpha(\vec{k})$, especially in the high-order terms which are anticipated to be fairly small $[O(r^{-3})]$. An alternative approach, which would eliminate much of the wrong temperature dependence in the approximate theories, is to determine $X(T)$ from the set of experimental results at the temperature $T$. That is, in fitting (2.1) to experimental results at a given temperature, the adjustable parameters now are

$$X, \; V_2/V_1, \; V_3/V_1, \; \ldots \quad . \tag{2.5}$$

In order to determine the $V_i$ values absolutely, the relation (2.2) must be used with $G_1(T)$ evaluated in a particular approximation. This would introduce additional inaccuracies and thus has not been attempted here.

## III. EXPERIMENTAL DATA

The reduced values of $\alpha(\vec{k})$ and also of the Fourier inverse of these, the $\alpha_i$ obtained by Moss[13] for $Cu_3Au$ at 405 and 450°C (presented in Table I),

probably represent an improvement over the earlier but classical values of Cowley,[14] in that allowance was made for size-effect and a temperature factor. Also, the intensities were calculated on an absolute basis to lessen the effect of parasitic scattering processes on the calculation.

A complete plot of $\alpha(\vec{k})$ in reciprocal space cannot be obtained because of the large thermal diffuse and Huang scattering in the region close to the fundamental reflection. However, by extrapolating his data to include this region, Moss[15] found he could obtain reasonably constant values for the $\alpha_i$ for several different forms of the extrapolation curve; the largest variation being shown by $\alpha_1$ and $\alpha_2$. In his calculation, Moss performed the Fourier inversion by using a summation over 1000 points of a symmetry cube in reciprocal space. The accuracy of the $\alpha_i$ values ($i = 1, \ldots, 11$) thus obtained is limited by the size of the grid used for summation. Conversely, if it is desired to reproduce the diffuse intensity all the $\alpha_i$ terms are really necessary, especially as $T$ approaches $T_c$.

In applying (2.1) to the experimental data, two factors must be considered. First, it is the values of $\alpha(\vec{k})$ in the region of the diffuse peak which are known most accurately. Second, if (2.1) is used directly to obtain $V(\vec{k})$ then a small error in $\alpha_{expt}(\vec{k})$ away from the diffuse peak, where $\alpha_{expt}(\vec{k})$ is small, will be propagated by (2.1) as a large error in $V(\vec{k})$.

In fitting the experimental results to theory, it is desirable, in view of the previous discussion, to choose a criterion of best fit which takes into account the accuracy of the experimental determination. One possible choice is to minimize

$$\Phi = \int w(\vec{k})[\alpha(\vec{k}) - \alpha_{expt}(\vec{k})]^2 d\vec{k} \qquad (3.1)$$

with respect to parameters (2.5), where $w(\vec{k})$ is a weighting factor which is related to the accuracy of the determination as a function of $\vec{k}$ and the integration is over the volume of reciprocal space for which the data were taken. However, the choice for $w(\vec{k})$ is not obvious.

TABLE I. Values of the Fourier coefficients $\alpha_i$ of the corrected diffuse scattering intensities obtained by Cowley and Moss for $Cu_3Au$ at the characteristic temperatures $T/T_c = 1.023$ and $T/T_c = 1.091$.

| Shell number | Lattice indices | Perfect order | $\alpha_i$ $T/T_c = 1.023$ | | $T/T_c = 1.091$ | |
|---|---|---|---|---|---|---|
| $i$ | $lmm$ | $(\alpha_i)_0$ | Cowley | Moss | Cowley | Moss |
| 1 | 110 | $-\frac{1}{3}$ | −0.152 | −0.218 | −0.148 | −0.195 |
| 2 | 200 | 1 | 0.186 | 0.286 | 0.172 | 0.215 |
| 3 | 211 | $-\frac{1}{3}$ | 0.009 | −0.012 | 0.019 | 0.003 |
| 4 | 220 | 1 | 0.095 | 0.122 | 0.068 | 0.077 |
| 5 | 310 | $-\frac{1}{3}$ | −0.053 | −0.073 | −0.049 | −0.052 |
| 6 | 222 | 1 | 0.025 | 0.069 | 0.007 | 0.028 |
| 7 | 321 | $-\frac{1}{3}$ | −0.016 | −0.023 | −0.008 | −0.010 |
| 8 | 400 | 1 | 0.048 | 0.067 | 0.042 | 0.036 |
| 9 | 330 | $-\frac{1}{3}$ | −0.026 | −0.028 | −0.022 | −0.015 |
| 10 | 411 | $-\frac{1}{3}$ | 0.011 | 0.004 | 0.020 | 0.007 |
| 11 | 420 | 1 | 0.026 | 0.047 | 0.025 | 0.015 |

## IV. REAL SPACE FORMALISM

An alternative approach is now outlined which should be computationally faster since it does not require the calculation of triple integrals, and also leads to a simpler choice for the weighting factor. In the discussion of Sec. II, a parallel development in terms of $\alpha_i$ and $V_i$ has been possible. The real space expression corresponding to (2.1), which is obtained by Fourier inversion of (2.1), is

$$[V(\vec{k}_m)/V_{o1}]X(T)(T/T_c)f(\alpha_{oi}) - \sum_j \alpha_{oj} V_{ij}/V_{o1} = 0, \quad i \neq 0 \qquad (4.1)$$

where the sum is over all sites in the lattice and

$$f(\alpha_{oi}) = (1/m_A m_B)\alpha_{oi} \qquad (4.2)$$

in the mean-field approximation.

A reasonable choice for the criterion of best fit is

$$\Phi_{min} = \sum_{i=1}^{11} w_i[\alpha_i(\text{expt}) - \alpha_i(\text{theory})]^2 , \qquad (4.3)$$

where $w_i$ is a weighting factor which is related to the estimated error in $\alpha_i$(expt). Clapp and Moss[3] chose $w_i = 1$ for $i = 1, \ldots, 11$. This choice is suitable if the $\alpha_i$(expt) have approximately the same absolute error. However, it can be seen from (1.4) that a given proportional error in $\alpha_{expt}(\vec{k})$ causes the same proportional error in all the $\alpha_i$; this is in keeping with the finding of Moss (see Sec. III) that varying the form of extrapolation for $\alpha(\vec{k})$ caused the values of $\alpha_1$ and $\alpha_2$, which are relatively large in magnitude, to vary the most. This suggests that a more appropriate choice for the $w_i$ is that they be inversely proportional to the squares of the absolute errors in the corresponding $\alpha_i$.

Clapp and Moss[3] effectively fitted the theory to $\alpha_1$ and $\alpha_2$. This would have some justification if it could be shown that most of the information about parameters (2.5) was contained in the values of these two terms. However, Paskin[16] has shown that the only significant differences in the theoretical values of the $\alpha_i$ produced by a long-range oscillatory interaction on the one hand and only a nearest-neighbor interaction on the other are in the higher-order $\alpha_i$. This is fairly obvious from (4.1) or (2.1), where it can readily be seen that $\alpha_i$ and $V_i$ are highly correlated (see, also, Ref. 3). Thus there is no justification for the assumption that most of the information about the high-order $V_i$ is contained in the low-order $\alpha_i$; rather the converse is true.

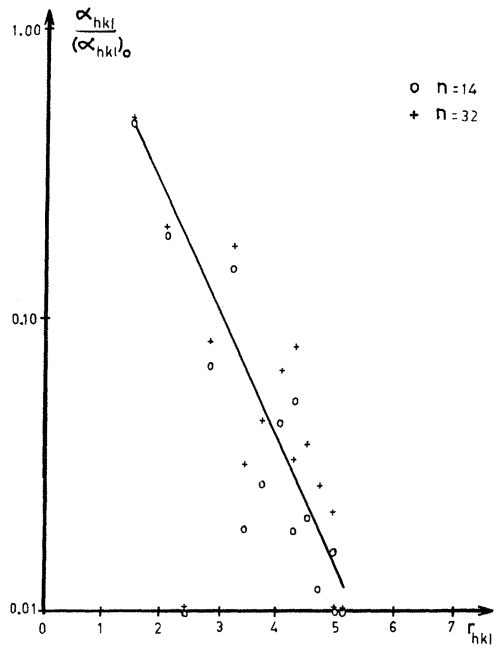


FIG. I. Comparison of the first fourteen $\alpha_i$ (as functions of distance in the lattice) obtained in the mean-field approximation with $n=14$ and $n=32$ variables in the solution. The results are for two interactions with $V_2/V_1 = -0.25$ at $T/T_c = 1.072$. The straight line indicates the average variation of $\alpha_i$ with distance.

## V. SOLUTION OF EQUATIONS

The numerical problem of refining the $\alpha_i$ data to obtain information about the pair-interaction ratios involves minimizing (4. 3), subject to the constraints (4. 1) in the first $m$ parameters (2. 5). A computer program has been written which takes the first $n$ variables $\alpha_i$ and obtains solutions with arbitrary values of the $m$ parameters. The mode of truncation chosen to obtain the $n$ by $n$ set of equations was, for $j > n$,

$$\alpha_j = \alpha_{n(\text{even})} \quad \text{for } j \text{ even}$$
$$= \alpha_{n(\text{odd})} \quad \text{for } j \text{ odd},$$

where $n$ (even) is the largest even shell not exceeding $n$, and $n$ (odd) is the largest odd shell not exceeding $n$.

Varying $n$, the number of $\alpha_i$ variables in the solution, for a given set of interactions, has been found to cause a slight shift in the solutions for the $\alpha_i$, but not to alter their general trend (see Fig. 1). The $\alpha_i$ values shift slightly toward the values for perfect order with increase in $n$. This resembles a temperature effect and indicates that some compensation for the finite value of $n$ may be included in the empirical determination of $X(T)$.

These considerations make it seem reasonable, as a first step, to choose $n=14$ for the subsequent investigations, so as to avoid using an excessive amount of computation time.

## VI. OPTIMIZATION METHOD

In this section we briefly describe the numerical solution scheme, which was chosen to solve the problem formulated in the previous section, of minimizing $\Phi$ with respect to the $m$ parameters (2. 5). For a given set of values of the $m$ parameters (4. 1) can be solved by linear or quasilinear techniques according to the particular approximation being considered. This yields

$$\alpha_i(X,\ V_2/V_1,\ V_3/V_1, \ldots), \quad \text{where } i = 1, \ldots, n,$$

which is combined with a powerful least-squares technique, based on the algorithm of Fletcher and Powell[17] to minimize $\Phi$ in the parameters (2. 5). Providing care is taken to avoid convergence problems, the method is quite efficient.

## VII. INITIAL ASSUMPTIONS

The two important assumptions which have been made in the following determinations of the first $m$ parameters (2. 5) are that $X(T)$ may be determined empirically and that $w_i$ is related to the accuracy of the measured values of the order parameters.

Following the discussion of Secs. III and IV, the test values which have been chosen for the $w_i$ are

$$w_1 \text{ and } w_2 = 0,$$
$$w_3, \ldots, w_{11} = 1.$$

That is, the experimental values of $\alpha_1$ and $\alpha_2$ are ignored. This set of values is of additional interest because it can be used to demonstrate the consistency of the experimental data and solution, since the determination of the parameters (2. 5) via (4. 1) implies values for $\alpha_1$ and $\alpha_2$ which may be compared (see Sec. IX) with the values contained in Table III.

For the sake of completeness, the effect of varying $w_i$ on the predicted values of the parameters is investigated in Sec. X.

Unless otherwise indicated, it is to be assumed that the relations (4. 1) and (4. 2) have been used with $X(T)$ determined empirically, taking $m=8$ and $n=14$ to fit the experimental data of Moss contained in Table I at the appropriate characteristic temperature.

## VIII. EFFECT OF VARYING DATA

The two major contributions to error in the reduced values of the diffuse intensities obtained by Moss are probably due to an additive constant background and to the factor used in the conversion to absolute intensities.[13] In his refinement of the measured intensities, Moss found that $\alpha_0 \neq 1$. He

TABLE II. Values of $X(T)$ and the first seven pair-interaction ratios $V_i/V_1$, where $i=2,\ldots,8$, obtained from the $\alpha_i$ data of Moss, the $\alpha_i$ data of Moss shifted by 10%, and $\alpha_i$ values obtained at random from the previous sets of data.

| | | $T/T_c=1.023$ | | | | | $T/T_c=1.091$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Data | | Moss | +10% | −10% | Rand 1 | Rand 2 | Moss | +10% | −10% | Rand 1 | Rand 2 |
| $X$ | | 1.001 | 0.994 | 1.011 | 0.987 | 1.008 | 0.986 | 0.976 | 0.997 | 0.984 | 0.991 |
| $i$ | $lmn$ | | | | | | | | | | |
| 2 | 200 | −0.175 | −0.187 | −0.204 | −0.173 | −0.151 | −0.208 | −0.206 | −0.214 | −0.270 | −0.243 |
| 3 | 211 | 0.061 | 0.034 | 0.054 | 0.115 | 0.035 | 0.027 | 0.021 | 0.032 | 0.039 | −0.004 |
| 4 | 220 | 0.099 | 0.090 | 0.079 | 0.231 | 0.090 | 0.073 | 0.080 | 0.062 | 0.109 | 0.049 |
| 5 | 310 | 0.005 | −0.017 | 0.009 | 0.092 | −0.013 | −0.055 | −0.073 | −0.035 | −0.010 | −0.102 |
| 6 | 222 | −0.056 | −0.079 | −0.042 | −0.125 | −0.120 | −0.062 | −0.077 | −0.050 | −0.074 | −0.066 |
| 7 | 321 | −0.001 | −0.009 | 0.002 | −0.001 | −0.016 | −0.013 | −0.016 | −0.010 | −0.007 | −0.020 |
| 8 | 400 | 0.042 | 0.041 | 0.043 | 0.050 | 0.044 | 0.022 | 0.020 | 0.024 | 0.023 | 0.020 |
| $\Phi_{\min}$ ($\times 10^5$) | | 0.51 | 0.76 | 0.47 | 3.5 | 6.6 | 0.11 | 0.16 | 0.07 | 0.03 | 0.85 |

corrected this by subtracting a fixed amount from each of the measured intensities. However, this is unnecessary because a constant background intensity will not alter the calculated $\alpha_i$ ($i\neq 0$) terms. If part of the error in the $\alpha_o$ value were caused by a proportional error in the conversion to absolute intensities then this would lead to a proportional error in the $\alpha_i$ (all $i$). The discussion in Sec. III and Ref. 11 makes an estimate of a 10% proportional error in the $\alpha_i$ seem reasonable. To investigate the effect such an error has on the determination of the pair-interaction ratios, we have chosen the following sets of $\alpha_i$ data at each temperature; the Moss values, the Moss values shifted toward and away from the values at perfect order by 10% of their magnitude, and two sets of data with each $\alpha_i$ value chosen at random from the previous three sets of data. In Table II, the values of the pair-interaction ratios, $V(r_{hkl})/V(r_{110})$, where $r_{hkl}=(h^2+k^2+l^2)^{1/2}$, together with the corresponding values of $X(T)$ and $\Phi_{\min}$, are presented for the various sets of $\alpha_i$ data.

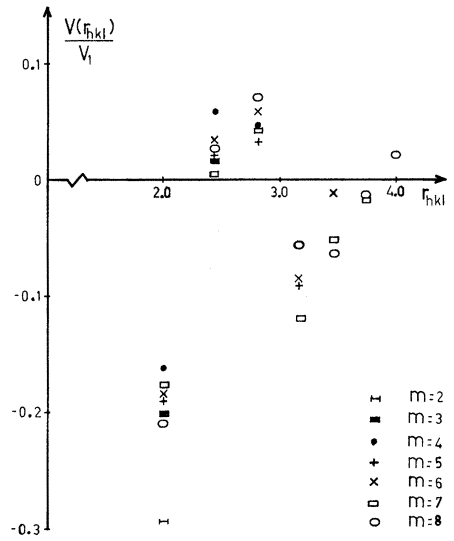


FIG. 2. Variation of the pair-interaction ratios with $m$, the number of interactions included in the determination. The results were obtained from the $\alpha_i$ data of Moss at $T/T_c=1.091$.

It can readily be seen that for the cases where all the $\alpha_i$ are shifted together, the main effect, as would be expected, is a temperature renormalization, whereas for the random cases, large changes in the interaction ratios can occur when compared with the values obtained from the Moss data. That is, the relative values of the $V_i$ are well determined by the relative values of the $\alpha_i$, and thus the results obtained by the present method should be quite accurate.

## IX. EFFECT OF INCLUDING MORE INTERACTION TERMS

It is desirable to investigate the effect of including more and more interaction terms, not exceeding the number of constraints in (4.3). If the values of the $m$ interactions calculated vary radically with increase in $m$, then little confidence could be assigned to any result. Alternatively, if there is a value of $m$ up to which the solution is stable but beyond which it varies radically, then this would have to be considered as being the limit to the number of meaningful parameters in the determination.

In Fig. 2, the effect of varying $m$ on the solution for the pair-interaction ratios is illustrated. It can be seen that the general oscillatory trend in the values of the pair-interaction ratios persists with increase in $m$ up to $m=8$. For $m=3$, the values are seen to agree closely with the results ($V_2/V_1=-0.200$ and $V_3/V_1=-0.015$) obtained by Clapp and Moss[3] for the same data but with different $w_i$.

In Table III, the values of the $\alpha_i$ for each value

TABLE III. Values of the first fourteen $\alpha_i$ terms for $m=2,\ldots,8$ interaction terms included in the determination of the pair-interaction ratios. The results were obtained from the data of Moss at $T/T_c=1.091$.

| Shell number $i$ | $\alpha_i$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $m=2$ | $m=3$ | $m=4$ | $m=5$ | $m=6$ | $m=7$ | $m=8$ | Moss expt |
| 1 | −0.155 | −0.158 | −0.164 | −0.186 | −0.189 | −0.197 | −0.186 | −0.195 |
| 2 | 0.192 | 0.189 | 0.200 | 0.233 | 0.238 | 0.250 | 0.239 | 0.215 |
| 3 | 0.003 | 0.004 | 0.002 | 0.004 | 0.004 | 0.006 | 0.003 | 0.003 |
| 4 | 0.070 | 0.071 | 0.071 | 0.077 | 0.076 | 0.077 | 0.077 | 0.077 |
| 5 | −0.048 | −0.048 | −0.048 | −0.049 | −0.049 | −0.050 | −0.052 | −0.052 |
| 6 | 0.022 | 0.023 | 0.023 | 0.022 | 0.023 | 0.024 | 0.028 | 0.028 |
| 7 | −0.010 | −0.010 | −0.009 | −0.011 | −0.011 | −0.010 | −0.009 | −0.010 |
| 8 | 0.044 | 0.043 | 0.044 | 0.039 | 0.040 | 0.039 | 0.036 | 0.036 |
| 9 | −0.018 | −0.018 | −0.018 | −0.012 | −0.011 | −0.012 | −0.015 | −0.015 |
| 10 | 0.004 | 0.004 | 0.003 | 0.002 | 0.001 | 0.0 | 0.007 | 0.007 |
| 11 | 0.023 | 0.023 | 0.022 | 0.022 | 0.021 | 0.020 | 0.016 | 0.015 |
| 12 | −0.005 | −0.005 | −0.005 | −0.004 | −0.005 | −0.006 | −0.006 | |
| 13 | 0.012 | 0.013 | 0.012 | 0.014 | 0.015 | 0.016 | 0.010 | |
| 14 | −0.003 | −0.003 | −0.003 | −0.004 | −0.005 | −0.005 | −0.002 | |
| $\Phi_{min}$ | $0.24\times10^{-3}$ | $0.22\times10^{-3}$ | $0.21\times10^{-3}$ | $0.14\times10^{-3}$ | $0.13\times10^{-3}$ | $0.12_6\times10^{-3}$ | $0.1\times10^{-5}$ | |

of $m$ are presented. The inclusion of higher-order interaction terms can be seen to lead to a significant improvement in the fit of the higher-order $\alpha_i$ terms ($\alpha_9$, $\alpha_{10}$, $\alpha_{11}$) to experiment, whereas $\alpha_3$ and $\alpha_4$ remain reasonably constant. This supports the hypothesis of Sec. IV.

It should be remembered at this point that $w_1$ and $w_2=0$, so that the agreement between the calculated and experimental values of $\alpha_1$ and $\alpha_2$ indicates that the determination is consistent with the complete data.

## X. VARIATION OF WEIGHTING FACTORS

The solution should be relatively insensitive to the precise values of the weighting factors $w_i$ since the choice for these is to a large extent arbitrary.

In Table IV, the pair-interaction ratios obtained with several different sets of weighting factors are presented. For *a*, *b*, and *c* the results are seen to be stable, whereas for *d* (corresponding to the choice made by Clapp and Moss) the values of the pair-interaction ratios with $m=8$ are seen to be significantly different. It has been demonstrated by the approach of Sec. IX, that the values of $V_i/V_1$ ($i=2,\ldots,m$) obtained with *d* are unstable for $m>3$ and so must be rejected. However, they agree very closely with the other values (*a*, *b*, *c*) for $m\leq3$. It should be noted that a reasonable estimate of the $w_i$ is that they are inversely proportional to the square of the absolute errors in the respective $\alpha_i$, so that the difference between *a*, *b*, and *c* is larger than might appear.

TABLE IV. Values of the first seven pair-interaction ratios for various choices of the weighting factors $w_i$, obtained from the data of Moss at $T/T_c=1.091$.

| Code | *a* | *b* | *c* | *d* |
|---|---|---|---|---|
| $w_1$, $w_2$ | 0.0 | 0.01 | 0.05 | 1.0 |
| $w_3,\ldots,w_{11}$ | 1.0 | 1.0 | 1.0 | 1.0 |
| Interaction ratios | | | | |
| $V_2/V_1$ | −0.208 | −0.211 | −0.198 | −0.157 |
| $V_3/V_1$ | 0.027 | 0.032 | 0.021 | 0.003 |
| $V_4/V_1$ | 0.073 | 0.072 | 0.051 | 0.016 |
| $V_5/V_1$ | −0.055 | −0.046 | −0.044 | −0.076 |
| $V_6/V_1$ | −0.062 | −0.055 | −0.056 | −0.038 |
| $V_7/V_1$ | −0.013 | −0.010 | −0.013 | −0.010 |
| $V_8/V_1$ | 0.022 | 0.024 | 0.024 | 0.013 |

## XI. COMPARISON OF PAIR-INTERACTION RATIOS AT DIFFERENT TEMPERATURES

The close agreement between the two sets of values of the interaction ratios for the Moss data in Table II has been taken as confirmation of the consistency of the data. No special temperature effects such as damping[18] are indicated, considering the accuracy of the determination.

## XII. COMPARISON WITH THE SCREENING INTERACTION IN THE FREE-ELECTRON MODEL

The determination of the pair-interaction ratios thus far has been independent of any assumed model for their prediction, so that an unprejudiced test of different models for the origin of the high-order interactions is possible.

An obvious model for trial is the free-electron screening model for pair interactions between ions. At large distances the form is given as[19,20]

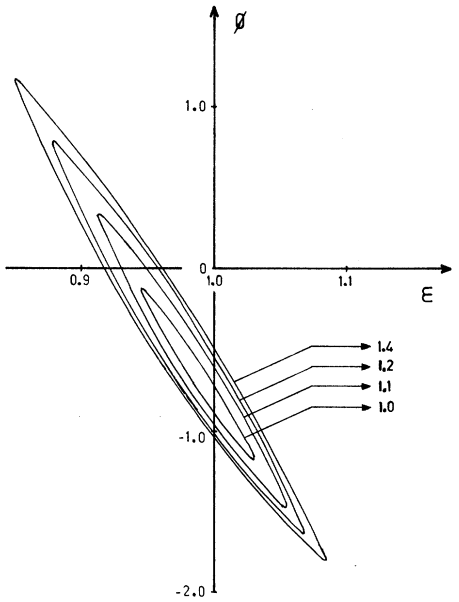


FIG. 3. Contours for the least-squares residual (relative values only) obtained by fitting the form $V(r_{hkl})/V_1 \sim A\cos(4.911_0\epsilon r_{hkl}+\phi)/(r_{hkl})^3$, where $\epsilon=(e/\text{at.})^{1/3}$, to the pair-interaction ratios obtained from the five sets of data at $T/T_c=1.091$ (see Table II). The results are for $A=1.9$.

$$V(r_{hkl})/V_1 = A\cos(2k_F a_0 r_{hkl}+\phi)/(r_{hkl})^3 , \qquad (12.1)$$

where $k_F$ is the Fermi momentum, $2a_0$ is the unit cell spacing. $A$ is here assumed to be a constant (independent of $k_F$), and $\phi$ is a phase factor.

The quantity $2k_F a_0$ may be related to the electron-per-atom ratio ($e$/at.) in the usual way.[21] Hence, it it is possible to write

$$V(r_{hkl})/V_1 \sim A\cos(4.911_0\epsilon r_{hkl}+\phi)/(r_{hkl})^3 , \qquad (12.2)$$

where $\epsilon=(e/\text{at.})^{1/3}$. This functional form has been fitted by least squares to the results contained in Table II. Various trial values of $A$ differing by 0.1 were used to plot contours of the least-squares residual as a function of $\epsilon$ and $\phi$. The contour plot for the value $A=1.9$, which yielded the minimum value for the results at $T/T_c=1.091$, is presented in Fig. 3. In Fig. 4, the pair-interaction curve which yielded the minimum value of the least-squares residual is plotted together with the empirical values.

The results for $Cu_3Au$ averaged over the two temperatures indicate

$$\epsilon_{\text{expt}} = 0.97 \pm 0.04$$

and

$$\phi_{\text{expt}} = 0.6 \pm 0.4 \ .$$

The value of $\epsilon_{\text{expt}}$ is in keeping with the normal one-electron-per-atom behavior of Cu and Au. However, the value of $\phi_{\text{expt}}$ differs significantly from the value ($\pm 0.0906$, the sign was undetermined) obtained by Kohn and Vosko.[22] This phase difference is of the same sign and magnitude as the phase shift of the asymptotic form (12.1) relative to the exact result for small $rk_F$ (see Ref. 19), at which distance the empirical values contained in Table II dominate the least-squares fit in the present calculation.

The good agreement of the results with (12.2) indicates that the long-range pair interactions in $Cu_3Au$ are fairly well predicted by the free-electron screening model. Indirectly, this provides strong evidence for the presence of a reasonably sharp cutoff in the occupation probability of the conduction-electron states in $\vec{k}$ space, in a concentrated disordered alloy ($Cu_3Au$), at temperatures $\simeq 700\,^{\circ}\text{K}$; that is, a well-defined Fermi surface.

## XIII. ADDITIONAL CONSIDERATIONS

Similar predictions for $V_i/V_1$ values calculated from experiment are found to obtain with $f(\alpha_i)$ in the Cowley theory.[23]

The Cowley data in Table I for $T/T_c=1.091$ has been found to lead to the following values of the interaction ratios:

$$V_2/V_1 = -0.195, \quad V_3/V_1 = -0.030,$$

$$V_4/V_1 = -0.030, \quad V_5/V_1 = -0.005.$$

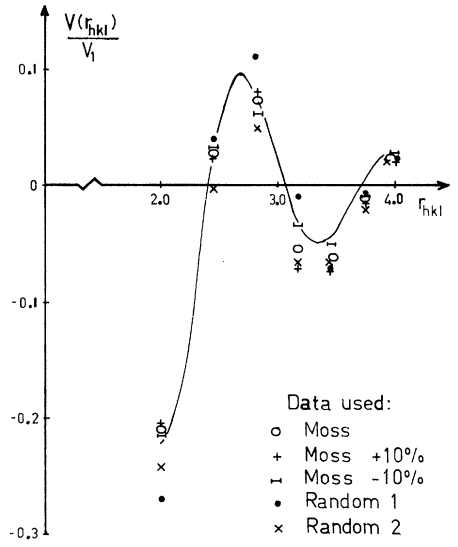


FIG. 4. Least-squares fit of the form $V(r_{hkl})/V_1 \sim A\cos(4.911_0\epsilon r_{hkl}+\phi)/(r_{hkl})^3$, where $\epsilon=(e/\text{at.})^{1/3}$, to the five sets of pair-interaction ratios obtained from the different sets of $\alpha_i$ data at $T/T_c=1.091$ (see Table II). The theoretical prediction for the interaction ratios is drawn as a continuous curve although it is only the values at the lattice sites $r_{hkl}$ which have significance here. The curve is for $A=1.9$, $\epsilon=0.98$, and $\phi=-0.7$.

Thus the improved accuracy of the Moss determination of the $\alpha_i$ is found to contain the information about the long-range oscillatory interactions.

The pair interaction (12.1) is based on the assumption of a spherical Fermi surface. If the Fermi surface has cylindrical or flat regions, then the interaction is of longer range in the directions perpendicular to these regions,[4,8,24] but with periodicity still proportional to $k_F$. Thus the determination of the values of the pair-interaction ratios provides a means of calipering the Fermi surface in all directions in reciprocal space, if a sufficient number of interaction terms is obtained (see also Ref. 25).

The Fermi surface for Cu(Ref. 26) has flat regions in the [100] and equivalent directions, this would account for the relatively large magnitude of $V_4/V_1$ in the present determination, if a similar Fermi surface is assumed for $Cu_3Au$.

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