

Moreover, the loss rate due to migration may be seen from Eq. (28) to take the form

$$dc_2/dt = -(3b/R^3)D_2c_2, \quad (40)$$

so that for the approximate steady state

$$\delta c_2/c_2 \sim (ba^2/56R^3)\Delta(T). \quad (41)$$

This shows that for Au at 300°K with $5b=R$, a separation of the sinks by $50a$ is sufficient to ensure the validity of Eq. (37). For Ag at room temperature, the analogous distance is some thousands of lattice spacings.

Finally, it is interesting to re-examine the work of de Jong and Koehler³ in the light of what we have found here. These authors study the growth of stacking fault tetrahedra under the assumptions: (a) that growth occurs by absorption at the corners of the tetrahedra at a rate found by assuming that the defect concentration is constant through the lattice, and (b) that the diffusion coefficient for voids is the local thermal-equilibrium value corresponding to the average defect concentration. The assumption (a) has previously been shown by

the author¹ to lead, in general, to a quite incorrect estimate of the defect loss rate. However, when one specifies a single atomic site as an infinite sink, this approximation leads to an erroneous estimate by only about a factor 2, because the gradients driving such a slow diffusion process are indeed almost negligible. Since, in this isolated case, the occupation probability of a potential defect site does not fall to zero at sites neighboring the sink, the averaging process involved in finding Eq. (21) from Eq. (13) does not occur, and the diffusion coefficient (13) may therefore be more appropriate than (31). Thus, provided the defect absorption occurs in regions of atomic dimensions near the tetrahedron corners, the assumptions made by de Jong and Koehler could give a reasonable description of the annealing.

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Effect of Long-Range Interactions on Order*

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Harrison and Paskin (HP) have calculated the ordering energy of β -CuZn using recent theoretical techniques of treating electron screening and Mott's polar model of an alloy. Good agreement is obtained between the calculated total energy of the order-disorder transformation and specific-heat measurements. A consequence of the HP calculation is that the ordering energy is long-range and oscillates in sign. Walker and Keating recently measured the neutron diffuse scattering of β -CuZn above the critical temperature T_c and find their data are in agreement with order calculated by only considering a nearest-neighbor interaction. Using the Cowley statistical theory of order, we compare the order generated by a nearest-neighbor interaction and the long-range interaction of HP at a temperature $1.1T_c$. We find the average behavior of the order generated by the nearest-neighbor and long-range interaction to be similar. The major difference is the nearest-neighbor interaction generates order that asymptotically, varies smoothly with neighbor distance whereas the order resulting from the long-range interaction fluctuates markedly about the nearest-neighbor generated order. This result may explain the success of statistical theories, based on nearest-neighbor interactions, in both order-disorder of alloys as well as in some magnetic systems which are also believed to have a similar long-range oscillatory interaction.

INTRODUCTION

HARRISON and Paskin¹ (HP) have calculated the ordering energy of β -CuZn using recent theoretical techniques of treating electron screening² and Mott's³ "polar model" of an alloy. Good agreement is obtained

between the HP calculation of the total energy of the order-disorder transformation and specific-heat measurements of this energy. A consequence of present screening calculations^{1,2} is the ordering energy is long-range and oscillatory. The magnitudes of even the far-neighbor ordering-energy terms are not negligible while the second-neighbor energy may be as high as 30% of the first-neighbor term. Walker and Keating⁴ recently measured the neutron diffuse scattering of β -CuZn. Although they do not obtain explicit order parameters,

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¹ A. Paskin, *Bull. Am. Phys. Soc.* **7**, 216 (1962); R. J. Harrison and A. Paskin, *J. Phys. Radium* **23**, 613 (1962).

² B. D. Silverman and P. R. Weiss, *Phys. Rev.* **114**, 989 (1959); W. Kohn and S. H. Vosko, *ibid.* **119**, 912 (1960); R. J. Harrison and A. Paskin, *J. Phys. Soc. Japan* **15**, 1902 (1960).

³ N. F. Mott, *Proc. Phys. Soc. (London)* **49**, 258 (1937).

⁴ C. B. Walker and D. T. Keating, *Phys. Rev.* **130**, 1726 (1963).

they find the over-all diffuse scattering is in agreement with calculations of the order propagated from a phenomenological nearest-neighbor interaction.

These observations would at first seem to be in contradiction with the HP ordering energy. Using Cowley's⁵ statistical theory of order, we here show that the long-range, oscillatory energy of HP yields about the same average behavior for the order parameters as does a simple nearest-neighbor interaction. The major difference is that the order parameters generated by the long-range interaction do not vary smoothly with distance whereas the nearest-neighbor interaction propagates order that asymptotically does vary smoothly with neighbor distance. We have thus shown how diffuse experiments that measure average properties of order in β -CuZn can be well approximated by a nearest-neighbor interaction even though the ordering energy may be of the long-range, oscillatory type found by HP. It is also pointed out that for magnetic systems having a long-range, oscillatory interaction energy, parallel arguments would lead us to expect the same results.

ORDERING ENERGY OF POLAR MODEL

In the polar model one considers the two types of atoms as point charges in a "sea" of conduction electrons. The magnitude of these point charges are taken to be the respective nuclear charges diminished by the average electronic charge within the atomic polyhedra surrounding the respective ions. The conduction electrons are at first assumed uniformly distributed throughout the alloy and the redistribution then calculated. For β -CuZn there are one and a half conduction electrons per polyhedron. The point charges to be shielded are then $(\frac{1}{2})e$ at the Zn site and $-(\frac{1}{2})e$ at the Cu site. Making use of recent screening calculations, HP find E , the electronic interaction energy arising from the interaction of these point charges with the screening electrons, is given by

$$E = \sum_{m>n} E_{m,n} = \sum_{m>n} eZ_n V(r_{mn}; Z_m). \quad (1)$$

Here $E_{m,n}$ is the interaction energy of ion pair m and n , V is the potential at site n due to the screening of the ion at site m , r_{mn} is the distance between sites, and Z_x is the difference between the ionic charge and the average number of conduction electrons per atomic polyhedron [i.e., $Z_x = \pm(\frac{1}{2})e$ in β -CuZn]. A reasonable representation for V in β -CuZn is found to be¹

$$V(r_{mn}; Z_m) = -\frac{eZ_m \alpha^2 \cos(2k_F r_{mn} + \phi)}{(2k_F)^5 (1 + \alpha^2/2)^2 r_{mn}^3}, \quad (2)$$

where k_F is the momentum of an electron at the Fermi surface (assumed spherical), $\alpha = q/2k_F$ where q is the usual Thomas-Fermi screening parameter, and ϕ is a

⁵ J. M. Cowley, Phys. Rev. **120**, 1648 (1960).

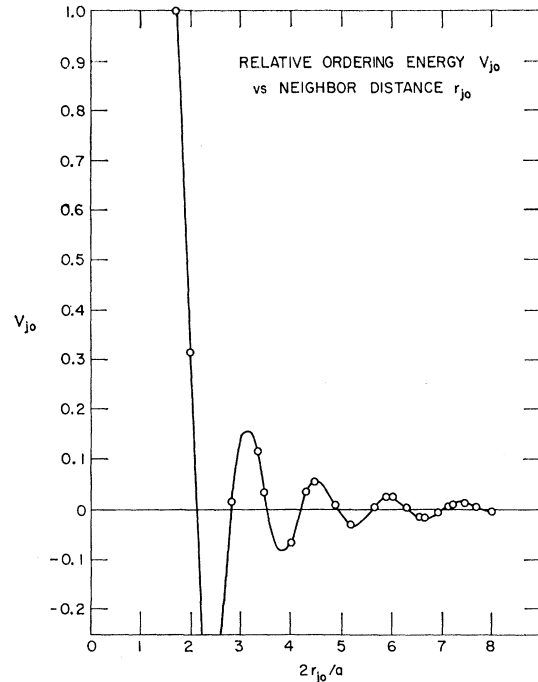


FIG. 1. The relative ordering energy V_{j0} as a function of r_{j0} the distance to the j th site. The energy is relative to the first-neighbor energy, for $\phi = \pi/2$, and distances are given relative to $a/2$ where a is the lattice parameter. The \circ 's indicate the j th neighbor values of V_{j0} .

phase factor to take into account deviations from the free-electron calculations.¹ From estimates of the energy of order-disorder, HP find a value of $\phi \sim \pi/2 + 0.28$ to be reasonable. This value of ϕ is close to the value for dilute solutions of Zn in Cu obtained by Blandin and Friedel^{6,7} (following Blatt) who give $\phi = 1.87$ rad. The major points to note for present considerations are: the pair interaction energy described by Eq. (2) is proportional to r_{mn}^{-3} and thus long-range, and the interaction is also oscillatory because of the cosine factor.

The phenomenological ordering energy⁵ of an AB alloy that usually appears in the statistical theories of order is

$$v_{mn} = (1/2)[E_{m,n}(A,A) + E_{m,n}(B,B)] - E_{m,n}(A,B), \quad (3)$$

where $E_{m,n}(X,Y)$ refers to energy of a pair of X and Y atoms at sites m and n , respectively. For AB alloys, on the basis of the polar model, $Z_n(A) = -Z_n(B)$, $E_{m,n}(A,A) = E_{m,n}(B,B) = -E_{m,n}(A,B)$, and the ordering energy is

$$v_{mn} = 2E_{m,n}(A,A) = 2e|Z_n|V(r_{mn}; |Z_m|). \quad (4)$$

In Fig. 1, the ordering energy (for $\phi = \pi/2$) relative to the nearest-neighbor energy is given as a function of the

⁶ A. Blandin and J. Friedel, J. Phys. Radium **21**, 689 (1960); Phys. Chem. Solids **17**, 170 (1960).

⁷ It disagrees with the value of ϕ obtained by Kohn and Vosko (Ref. 2), who, however, point out their technique could not match the resistivity data for Zn in Cu.

neighbor distance in units of $a/2$, where a is the lattice parameter. The important points to note are: the second-neighbor interaction is about 30% of the nearest neighbor for this interaction and more distant neighbors still give finite contributions (e.g., the eighth neighbor is about 5% of the first neighbor).

Because of the range and magnitude of the ordering energy, one might expect that statistical treatments based on a nearest-neighbor interaction would need serious modification. Fortunately, it seems that the oscillatory nature of the interaction tends to cause the more distant neighbors in effect to nullify one another, and allow the nearest-neighbor approximation to be a good description. This is demonstrated in the next section.

ORDER PARAMETERS WITH LONG-RANGE INTERACTION

Of the various statistical theories of order available, the Cowley theory⁵ is most convenient for examining the relative effects of the long-range ordering energy on the order parameters above the critical temperature T_c . The basic equations⁵ relating the order parameter α_j and the interaction energy for an AB alloy are

$$\sum_j v_{ij}\alpha_j + 2kT\alpha_i^{-1} \int \ln[(1+\alpha_i)/(1-\alpha_i)]d\alpha_i = 0. \quad (5)$$

Here $\alpha_j = 1 - 2P_{AB,j}$ where $P_{AB,j}$ is the probability of finding an AB pair as j th neighbors, k = Boltzmann's constant, and v_{ij} is the ordering energy of Eq. (4). If we define v_{i0} as the n th-neighbor ordering energy and note for $\alpha_i \ll 1$, $\int \ln[(1+\alpha_i)/(1-\alpha_i)]d\alpha_i \cong \alpha_i^2$, Eq. (5) may be written as a linear set of difference equations

$$\sum_j V_{ij}\alpha_j + b\alpha_i = -V_{i0}, \quad (6)$$

where $V_{ij} = v_{ij}/v_{10}$ or all interaction energies are in terms of the nearest-neighbor energy v_{10} and V_{j0} is the relative interaction energy of the j th neighbor. The parameter

$$b = (2kT_c/v_{10})(T/T_c), \quad (7)$$

may be evaluated in terms of the Cowley theory by noting that the critical temperature of Eq. (5) is related to the first N terms of the ordering energies as follows:

$$(2kT_c/v_{10}) = - \sum_{j=1}^N V_{j0}z_j. \quad (8)$$

Here z_j is the coordination number of the j th neighbor times the sign of the order parameter α_j for perfect order. Making use of Eqs. (6), (7), and (8), we may vary the number of terms and magnitudes of the ordering energies and examine the variation in the order parameters for a fixed T_c . We have evaluated the first forty values of α_j at $T/T_c = 1.10$ (a temperature of

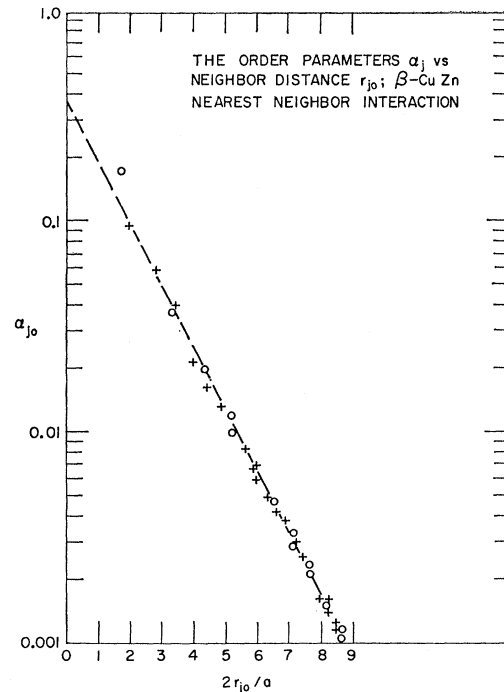


FIG. 2. The order parameters α_j versus neighbor distance r_{j0} for β -CuZn at $T/T_c = 1.10$. The + and \circ symbols indicate positive and negative values of α_j , respectively. Only a nearest-neighbor ordering energy is considered.

interest for comparison with the experimental results of Walker and Keating⁴). The linear set of equations of (6) were solved numerically for a nearest-neighbor interaction and keeping the first forty ordering-energy terms of Eq. (4) for $\phi = \pi/2 \pm 0.28$ and $\pi/2$.

We have examined the accuracy of the procedure of solving the difference equations keeping the first N terms in α_j and setting the remainder equal to zero. The results obtained from a nearest-neighbor interaction keeping the first thirty terms are compared with those obtained keeping the first forty terms. The magnitude of the differences between the two sets of order parameters increases monotonically with increasing neighbor distance. The relative differences are negligible until about the fifteenth neighbor, have increased to about ten percent by the twentieth neighbor, and have reached thirty percent by the thirtieth neighbor. This indicates that meaningful comparisons of the first thirty-order parameters may be made on results obtained keeping the first forty terms in α_j . In Fig. 2 the results for the nearest-neighbor interaction are given.⁸ In Fig. 3 the results are given for the long-range interaction with

⁸ It might be noted that these values are somewhat smaller than those given by Cowley (Ref. 5). The asymptotic solution of Eq. (6) is readily found to be $|\alpha_j| = Cr_{j0}^{-1} \exp(-fr_{j0})$, where $f = a^{-1}(b-8)^{1/2}$ for β -CuZn. Comparing Cowley's results with the present results and the asymptotic expression for α , it is apparent that Cowley's order parameters in Table II for $kT/V_1 = 4.4$ are in error.

$\phi = \pi/2$. The general results for the other ϕ 's are similar to those given in Fig. 3, although the relative values of the first- and second-neighbor interaction varies markedly for the three cases. We see that the nearest-neighbor interaction is well represented on the semilogarithmic plot of Fig. 2 by a straight line⁹ over most of the range shown here (i.e., about the first 30 neighbors). The long-range-interaction order parameters on the average lie somewhat above the same straight line describing the average of the nearest-neighbor-generated order parameters but there are large variations in specific order parameters.

We have also examined the effect of temperature on the relative order. The general results are the same at $T/T_c = 1.235$ as at $T/T_c = 1.10$ except that the fluctuations at the higher temperature have actually caused a reversal in the sign of some of the far-neighbor order parameters. At $T/T_c = 1.10$ the order parameters have the same sign as the order parameters do below the critical temperature where long-range order exists. A neighboring site that had an *A* atom on it for perfect order still prefers an *A* atom at temperatures immediately above the critical temperature both for the nearest-neighbor and long-range interactions. At $T/T_c = 1.235$, the nearest-neighbor order is still of the same type as below the critical temperature, whereas the long-range interaction favors the opposite atom type at some sites beyond the thirteenth neighbor. As the order at the higher temperatures is smaller and relatively less important, no attempt was made to study further the order reversal at higher temperatures arising from the long-interaction. In any event, the general results at the two temperatures are the same: the average order generated by the nearest-neighbor and long-range oscillatory interaction is approximately the same except that long-range order produces marked fluctuations in order about the average. Thus, we see measurements such as those of Walker and Keating⁴ which reflect the average state of order may be well approximated by a nearest-neighbor interaction even though the interaction may in fact be the long-range interaction described here. The only way of distinguishing between the two would be to look at the order parameters themselves and see if they do indeed fluctuate about a smooth curve as predicted by the long-range interaction or whether they are the well-behaved parameters predicted by a nearest-neighbor interaction.

In the light of the fact that long-range oscillatory

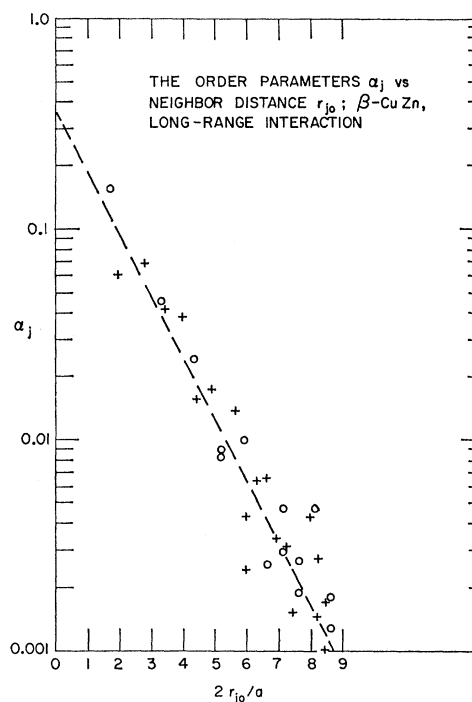


FIG. 3. The order parameter α_j versus neighbor distance for β -CuZn at $T/T_c = 1.10$. The + and o symbols indicate positive and negative values of α_j , respectively. The first forty neighbor ordering energies of HP ($\phi = \pi/2$) are kept. The dashed line is the average order obtained from keeping only the nearest-neighbor ordering energy.

interaction also arise in other phenomena¹⁰ involving electron interactions, it is tempting to generalize the conclusions indicated by the order-disorder results. It might therefore be expected, in general, that cooperative effects arising from long-range interactions of the form given here will, on the average, be well approximated by nearest-neighbor statistical treatments. For example, the parallel statistical treatments of order-disorder¹¹ and spin or magnetic disorder,¹¹ suggest that magnetic systems having similar long-range oscillatory interactions¹⁰ will have magnetic critical scattering which, on the average, will also be well described by a nearest-neighbor approximation. On the other hand, if one is interested in the effects of a long-range oscillatory potential this suggests that one should look for appropriate fluctuations in the detailed behavior of the critical scattering arising from alloy or magnetic disorder.

⁹ The semilog plot of the ordering parameter as a function of r_{j_0} should be approximately a straight line on the basis of the asymptotic expression given in Ref. 8.

¹⁰ M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954). T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956); K. Yosida, Phys. Rev. **106**, 893 (1957).

¹¹ R. J. Elliot and W. Marshall, Rev. Mod. Phys. **30**, 75 (1958).