Order-Disorder of Nonstoichiometric Binary Alloys and Ising Antiferromagnets in Magnetic Fields*

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High-temperature expansions of the free energy of Ising ferro- and antiferromagnets on the square, simple cubic, and body-centered cubic lattices have been derived directly from the corresponding low-temperature expansions using a generalization of the technique proposed by Domb. These lattices, being loose-packed, can be divided into two identical sublattices, α and β, such that every α site has only β sites as nearest neighbors. The high-temperature expansions treat the finite magnetic fields and magnetic moments on the α and β sites as independent quantities. With these series, which extend to eleventh order in the appropriate energies divided by kT, the high-temperature expansions of the magnetization and the logarithmic derivative of the staggered susceptibility have been developed. Padé approximants to these series are used to obtain the critical temperature and the magnetization at the critical temperature as a function of applied magnetic field. These are used to determine the order-disorder critical temperature of nearest-neighbor interaction binary alloys as a function of composition. The results are in good agreement with the observed values for β-brass at constant pressure. When the experimental values are corrected for the variation of lattice parameter with composition, the agreement is quite poor. It is concluded that a single volume-dependent order-disorder interaction energy is insufficient to describe the transition over the range of compositions in which it is observed.

I. INTRODUCTION

IT is well known that the approximate solutions for the thermodynamic properties of binary alloys which show order-disorder transitions tend to disagree with experimentally determined parameters in at least one of two systematic manners. The simplest approximation, due to Bragg and Williams,[1] focuses attention on the long-range order only and, consequently, does not predict the observed specific heat associated with the breakdown of short-range order above the critical temperature, T_c. Theories which take the short-range order into account, such as the Bethe-Peierls[2] theory, do show this high-temperature specific heat. In general, however, the experiments indicate that the disordering takes place over a significantly smaller temperature region, below T_c, than is predicted by the theories. This is particularly true when the transitions are of higher than first order.

There are two possible types of causes for these discrepancies. The first is an important failure of the physical model used in the calculations. It is generally assumed in the calculations that the dominant interactions which control the thermodynamics of the order-disorder process are nearest-neighbor interactions, and that the process can be considered to take place at constant volume. Various authors have obtained improved agreement with experiment by taking into account longer range interactions,[3] the thermal expansion,[4] and the change of the vibrational spectrum with changes in the state of order.[5] On the other hand, it is possible that the primary source of the disagreement between theory and experiment is the nature of the mathematical approximations. Wannier's[6] comparison of the approximate solutions, for this model, with the exact solution in two dimensions of Onsager[7] shows that the mathematical approximations themselves tend to spread out the temperature range of disordering below T_c. Thus, the large improvements obtained in the calculated thermodynamic properties by inclusion of longer range interactions, thermal expansion, and the changes of the vibrational spectrum may only be the result of an unjustified fitting of parameters to poor mathematical approximations. Since the situation has been described beautifully by Guttman in Sec. 16 of his review article,[8] this point will not be further labored. The question then of determining, in a reliable manner, which are the dominant causes of the discrepancies between theory and experiment is of paramount importance in the theory of these processes.

This paper describes one of a series of experimental and theoretical investigations which should yield more insight into this problem. It is designed to take advantage of two recent theoretical advances in the study of the Ising model. The first of these is the development of methods of deriving and studying the high- and low temperature expansions of the partition functions. These developments were put forth in a large number

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[1] W. L. Bragg and E. J. Williams, Proc. Roy. Soc. (London) **A145**, 699 (1934); **A151**, 540 (1935).
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of papers, primarily from the King's College, London group of Domb, Fisher, Sykes and co-workers, and are partially described in the review article of Domb.[9] The second is a further advance in the study of the expansions, known as the method of Padé approximants, whose use has been justified and developed primarily by Baker,[10] along with the King's College group. As a result of these advances, it is now possible to locate, with a reasonably high degree of accuracy, the critical temperatures associated with various physical models for the order-disorder process, if it is *known* that some physical property diverges at T_c like $[1-(T/T_c)]^{-\gamma}$, where γ may be unknown, and if a sufficient number of terms of the appropriate high- or low-temperature expansion of that property are known. In addition, it is possible to obtain fairly reliable values of physical properties which vary slowly with temperature using the Padé approximants to the appropriate series expansions.

A particularly convenient parameter for study by these techniques is the composition dependence of the order-disorder critical temperature. As is shown below, calculation of this parameter simply involves the determination of the variation of the Ising antiferromagnet T_c with applied magnetic field, and the value of the magnetization at this T_c. The results of the first part of this program, for the square, simple cubic, and bcc lattices, have been published previously.[11] In this paper, those results and their calculations are discussed in more detail, and the results of the second portion of the program are presented. Finally, the implications of the results of the calculations are discussed.

II. THE PHYSICAL MODEL AND ITS RELATION TO THE ISING MODEL

The relationship between the Ising model of antiferromagnetism and the binary alloy problem has been presented by a number of authors.[12] In this section we present definitions and relations which will be needed later.

We consider a system with N atoms and lattice sites, N_A atoms of type A and N_B of type B, where

$$N_A+N_B=N. \tag{2.1}$$

The lattice is taken to be loose-packed, so that it can be split into identical sublattices, α and β, such that every nearest neighbor of a site on the α sublattice is on the β sublattice. The energy of any configuration is then given by

$$E=N_{AB}V+N_AV'+\tfrac{1}{2}(zNV_{BB}), \tag{2.2}$$

where

$$V=V_{AB}-\tfrac{1}{2}(V_{AA}+V_{BB}) \tag{2.3}$$

and

$$V'=\tfrac{1}{2}[z(V_{AA}-V_{BB})]. \tag{2.4}$$

Here, N_{AA}, N_{BB}, and N_{AB} are the number of A-A, B-B, and A-B nearest-neighbor pairs, respectively, and V_{AA}, V_{BB}, and V_{AB} are the associated pairwise interaction energies.

Equation (2.2) yields the energy of any configuration as a linear combination of the three variables N_{AB}, N_A, and N. Since N is the same for all configurations, we may normalize the energy to eliminate the third term of Eq. (2.2).

The conversion to the Ising model is then performed by introduction of the variable σ_i where

$$\begin{aligned}\sigma_i&=+1 \quad \text{for an } A \text{ atom on site } i,\\ &=-1 \quad \text{for a } B \text{ atom on site } i.\end{aligned} \tag{2.5}$$

In addition, we chose to work with an ensemble in which all possible values of N_A and N_B consistent with a fixed N are allowed. In this case, the partition function is given by

$$Z=\sum_{\sigma_i=\pm1}\cdots\sum_{\sigma_N=\pm1}\exp[(J/kT)\sum_{\langle i,j\rangle}\sigma_i\sigma_j-(mH/kT)\sum_i\sigma_i]. \tag{2.6}$$

Here, the angular brackets $\langle i, j\rangle$ indicate that the summation is over nearest-neighbor sites, and

$$J=\tfrac{1}{2}V. \tag{2.7}$$

H is determined by the condition

$$M/m=-(kT/m)(\partial \ln Z/\partial H)=\sum_i\sigma_i=2N_A-N, \tag{2.8}$$

where M is the expectation value of the magnetization and m is the magnetic moment per spin.

The justification for the use of such an ensemble is, as usual, that only configurations with the desired value of M contribute appreciably to the partition function in the thermodynamic limit. Since, however, we are dealing with a critical phenomenon, this should be proved explicitly.

If the fluctuations are to be small, then we expect $(\langle M^2\rangle-\langle M\rangle^2)/\langle M\rangle^2$ to be of the order $1/N$. It is easily shown that

$$\langle M^2\rangle-\langle M\rangle^2=-kT\chi_T, \tag{2.9}$$

where χ_T is the isothermal susceptibility of the Ising antiferromagnetic system. Thus, the fluctuations will be small if χ_T remains finite at T_c. The work of Sykes and Fisher[13] indicates that this is the case at $H=0$. They find that $\partial\chi_T/\partial T=\infty$ at T_c, but that χ itself remains finite. This work is based on studies of finite numbers of terms of the high-temperature series expansions of the partition function. Similarly, Ziman's[14]

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[12] See, e.g., Kerson Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), Ch. 16.
[13] M. F. Sykes and M. E. Fisher, Physica **28**, 919 (1962); **28**, 939 (1962).
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Bethe–Peierls analysis of the Ising system indicates that χ_T remains finite at T_c (>0°K) for finite H. On the basis of these studies, we will assume that χ_T is finite at T_c, so that Eq. (2.8) does correctly yield the composition and that spin configurations corresponding to other compositions make a negligible contribution to the partition function.

III. ISING ANTIFERROMAGNET IN A MAGNETIC FIELD

As indicated above, the calculation consists of two parts. The results of the first part, the calculation of the magnetic field dependence of T_c, have been presented in an extended abstract elsewhere.[11] Since the methods of obtaining the results and their accuracies were not described in sufficient detail, we present some necessary additions here.

To determine the critical temperature with a high degree of accuracy with the Padé approximants it is valuable to study a series expansion of a physical parameter which diverges at the critical temperature like $[1-(x/x_c)]^{-\gamma}$ where x is the power series variable, x_c is its value at the critical temperature, and $\gamma \geq 1$. For the reasons presented by Rushbrooke and Wood,[15] we chose the staggered susceptibility and assumed that these reasons remained valid for the Ising antiferromagnet in finite H.

To obtain the staggered susceptibility, it is necessary to generalize the Hamiltonian from that which led to Eq. (2.6) to one of the form

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H_\alpha m_\alpha \sum_{i \text{ on } \alpha} \sigma_i - H_\beta m_\beta \sum_{i \text{ on } \beta} \sigma_i. \quad (3.1)$$

Our procedure then is to derive a high-temperature expansion for the Helmholtz free energy per spin on the square, simple cubic, and bcc lattices with the Hamiltonian of Eq. (3.1), to obtain a staggered susceptibility from this free energy, and to use the Padé approximants to determine the locations of the singularities.[16]

Our task is considerably simplified, however, because Sykes, Essam, and Gaunt[17] [hereafter denoted as (SEG)] have recently presented an elegant method for obtaining the low-temperature expansions of the free energy for the Hamiltonian. In this paper the low-temperature expansions obtained from their work are used to derive the high-temperature expansions. The resulting high-temperature expansions are more generally applicable than the low-temperature expansions from which they were obtained. To make this clear, the nature of the low-temperature expansions must be examined.

A. The Low-Temperature Expansions

The nature of the low-temperature expansions of (SEG) is readily visualized. Consider the Hamiltonian of Eq. (3.1). For $J>0$, $m_\alpha = m_\beta$, and $H_\alpha = H_\beta$, the coupling is ferromagnetic and the ground state is one in which all the spins are aligned parallel to the magnetic field. Excited states of the system can be grouped in terms of the number of overturned spins, leading to a low-temperature expansion in powers of the variables

$$\mu = \exp(-2m_\alpha H_\alpha / kT), \quad (3.2)$$

$$\nu = \exp(-2m_\beta H_\beta / kT), \quad (3.3)$$

and

$$u = \exp(-4J/kT). \quad (3.4)$$

For antiferromagnetic coupling, a spatially constant magnetic field ($H_\alpha = H_\beta$), and $m_\alpha = m_\beta$, the problem is a bit more complicated. There exists a critical field, H_c, such that $H<H_c$ implies an antiferromagnetic ground state, and $H>H_c$ implies a ground state in which all the spins are aligned parallel to the magnetic field. This critical field is easily shown to be given by

$$H_c = -\gamma J / m_\alpha, \quad (3.5)$$

where γ is the number of nearest neighbors of any lattice point.

The existence of these two unique ground states implies the existence of two forms for the low-temperature expansion. For $H<H_c$, the expansion is in terms of spins overturned from the antiferromagnetic ground state, while for $H>H_c$, the expansion is in terms of spins overturned from the parallel spin ground state.

Finally, there is the case in which the magnetic field is staggered. That is, the sign of the magnetic field is, say, positive on α sites and negative on β sites. In this case, there is a unique antiferromagnetic ground state for all values of H, and $J<0$. For $J>0$, the ferromagnetic ground state remains for $H<H_c$, while an antiparallel arrangement comprises the ground state for $H>H_c$.

As long as $H<H_c$, the ground states are determined by the sign of J. Thus, for arbitrary H_α's and H_β's, whose magnitude is less than H_c, we need not know the magnitude or sign of H_α and H_β to determine the ground state and the form of the low-temperature expansion. Moreover, the ferro- and antiferromagnetic problems can be brought into complete equivalence by changing the spin variable on one sublattice. That is, for $J<0$, we can set

$$\sigma_\alpha' = -\sigma_\alpha$$

and

$$J' = -J. \quad (3.6)$$

The Hamiltonian, expressed in terms of σ_α', σ_β', and J' is completely equivalent to the ferromagnetic Hamiltonian expressed in terms of σ_α, σ_β, and J.

As a result of this equivalence, (SEG) derive a general low-temperature expansion for the Ising spin

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[16] C. Domb and M. F. Sykes, J. Math. Phys. **2**, 63 (1961).
[17] M. F. Sykes, J. W. Essam, and D. S. Gaunt, J. Math. Phys. **6**, 283 (1965).

system for the general case of $H_\alpha \neq H_\beta \neq 0$. It is understood that when H_α, H_β, and J have the appropriate signs, the corresponding magnetic fields are less than H_c. Thus, in establishing a relationship with this expansion, we may consider the case in which J, H_α, and H_β are all positive. It is convenient to work with a system containing N spins per sublattice, and to write Eq. (3.1) as

$$\mathcal{H} = E_0 + \mathcal{H}', \tag{3.7}$$

where the ground-state energy is

$$E_0 = -JNz - NH_\alpha m_\alpha - NH_\beta m_\beta. \tag{3.8}$$

The free energy per spin can then be written as

$$F = E_0/2N - (kT/2)\ln\Lambda, \tag{3.9}$$

where

$$\ln\Lambda = N^{-1}\ln \sum_{\text{configurations}} \exp(-\mathcal{H}'/kT). \tag{3.10}$$

Then $\ln\Lambda$ defined by Eq. (3.10) is almost equivalent to that used in Sec. 3 of (SEG). The low-temperature expansion of $\ln\Lambda$ then takes the form

$$\ln\Lambda = \sum_{i=1}^{\infty}\sum_{j=0}^{i} f_{i-j,j}(u)\mu^{i-j}\nu^j, \tag{3.11}$$

with

$$f_{j,k} = f_{k,j}. \tag{3.12}$$

The $f_{i-j,j}(u)$ can be calculated directly from the generating relations presented by (SEG) to orders which are determined, for each structure, by the completeness of the enumeration of diagrams. We have calculated the $f_{i-j,j}$ to order 5 in j using data in (SEG). Sykes later supplied us with the $f_{i-j,j}$ to order 6.

B. The High-Temperature Expansions

For certain applications of these expansions, which will be discussed below, it is convenient to work with high-temperature, rather than low-temperature, expansions of $\ln\Lambda$. Sykes has shown,[18] in analogy with the case $H_\alpha = H_\beta$,[19] that the high-temperature expansion has the general form

$$\ln\Lambda = \ln(1+\mu)(1+\nu) + \sum_{\lambda=1}^{\infty}\frac{(u-1)^\lambda}{\lambda!}\frac{\phi_\lambda(\mu,\nu)}{[(1+\mu)(1+\nu)]^\lambda}. \tag{3.13}$$

In this expression, $\phi_\lambda(\mu,\nu)$ has the general form

$$\phi_\lambda = \sum_{i=1}^{\lambda}\sum_{j=0}^{i} a_{i-j,j}{}^\lambda(\mu^{i-j}\nu^j + \mu^{\lambda-i-j}\nu^{\lambda-j}), \tag{3.14}$$

where the symmetry of the problem implies that

$$a_{i-j,j}{}^\lambda = a_{j,i-j}{}^\lambda. \tag{3.15}$$

Since the ϕ_λ have this form, a knowledge of the low-temperature expansion to a given order is sufficient for generating the high-temperature expansion to the same order. To obtain the ϕ_λ's, we differentiate Eq. (3.11) n times with respect to u, and to evaluate the result at $u=1$. We obtain

$$\left.\frac{\partial^n \ln\Lambda}{\partial u^n}\right|_{u=1} = \sum_{i=1}^{\infty}\sum_{j=0}^{i}\mu^{i-j}\nu^j \left.\frac{d^n f_{i-j,j}}{du^n}\right|_{u=1}. \tag{3.16}$$

Similarly, from Eq. (3.13),

$$\partial^n \ln\Lambda/\partial u^n\,|_{u=1} = \phi_n(\mu,\nu)/[(1+\mu)(1+\nu)]^n. \tag{3.17}$$

Combining Eqs. (3.14), (3.16), and (3.17), we get

$$\frac{\sum_{i=1}^{n}\sum_{j=0}^{i} a_{i-j,j}{}^n(\mu^{i-j}\nu^j + \mu^{n-i+j}\nu^{n-j})}{[(1+\mu)(1+\nu)]^n} = \sum_{i=1}^{\infty}\sum_{j=0}^{i}\mu^{i-j}\nu^j \left.\frac{d^n f_{i-j,j}}{du^n}\right|_{u=1}. \tag{3.18}$$

Equation (3.18) should be viewed with extreme caution. We are equating power series which are valid for different values of T. It is highly likely that there are points of nonanalyticity of the functions which these power series represent. Nevertheless, physically, there is one situation in which we expect the regions to overlap. Let H_α and H_β differ by infinitesmal quantities and $mH_\alpha \gg kT$, where $H_\alpha > 0$. Then, for very small J (i.e., $u \approx 1$) the low-temperature expansion around the ferromagnetically ordered ground state should be valid for both positive and negative J. In this case, both μ and ν are small quantities. Under the same circumstances, the high-temperature expansion of Eq. (3.13) owes its convergence to the small value of $(u-1)$. In this case, the denominator of the left-hand side of Eq. (3.18) can be expanded by means of the binomial theorem to yield

$$\sum_{i=1}^{n}\sum_{j=0}^{i}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty} a_{i-j,j}{}^n(\mu^{i-j}\nu^j + \mu^{n-i+j}\nu^{n-j})\binom{-n}{l}\binom{-n}{k}\mu^k\nu^l = \sum_{i=1}^{\infty}\sum_{j=0}^{i}\mu^{i-j}\nu^j \left.\frac{d^n f_{i-j,j}}{du^n}\right|_{u=1}. \tag{3.19}$$

Here,

$$\binom{-n}{l} = \frac{(-n)(-n-1)\cdots(-n-l+1)}{l!}. \tag{3.20}$$

The coefficients $a_{i-j,j}{}^n$ have been determined by matching powers of μ and ν on the two sides of Eq. (3.19). The coefficients so obtained are tabulated in Appendix A. It should be noted that although there are an infinite number of equations resulting from Eq. (3.19), there are only $n(n+3)/2$ variables $a_{i-j,j}{}^n$. Of these variables, only slightly more than one-half are independent, as a result of Eq. (3.15). These

[18] M. F. Sykes (private communication).
[19] C. Domb, Proc. Roy. Soc. (London) **A199**, 199 (1949).

coefficients are determined by a knowledge of the $(d^n f_{i-j,j}/du^n)$ evaluated at $u=1$, for values $i \leq n$.

For Eqs. (3.13) and (3.14) to be correct forms for the high-temperature expansions, the remainder of the equations associated with Eq. (3.19) must be satisfied as well. Since we know the low-temperature expansions to some finite order, $i=m$, the validity of Eq. (3.13) can only be checked to that order. The checks have always indicated that Eq. (3.19) is satisfied. Thus, the high-temperature expansions are determined and correct to order m.

It has been claimed above that the high-temperature expansions are of more general validity than the low-temperature expansions from which they were derived. This statement appears to contradict the fact that they were derived from a low-temperature expansion in which the magnetic field was strong ($mH \gg kT$) and of a form which reinforced the tendency to order in a ground state determined by the sign of J. The reason for the generality is as follows. The high-temperature expansion owes its convergence entirely to the fact that mH_α, mH_β and J are very much less than kT. In its final form, i.e., in powers of mH_α/kT, mH_β/kT, and J/kT, it is purely a function of the geometry of the lattice. There is no difference in the form of the series for, say, $J<0$ or $J>0$ until explicit values of J are used. Similarly, for sufficiently large T, the magnitude or form (staggered or uniform) of the magnetic field does not change the coefficients of the series. This is because the high-temperature expansion is strictly an expansion in interaction energies divided by kT. In contrast to this the low-temperature expansion depends on the energy ordering of the states.

C. Determination of the Magnetic Field Dependences of the Critical Temperatures

It is implicitly assumed in this work that the transition from an ordered to disordered state characteristic of the zero-field case exists for finite uniform magnetic fields less than H_c, and that the staggered susceptibility, χ_h, diverges at T_c with a form $[1-(T_c/T)]^{-\gamma}$ for $T \geq T_c$. In this case, the techniques of Baker[10] can be used directly to determine the value of T_c.

To obtain the staggered susceptibility, we write

$$\epsilon = \exp(-2mH/kT), \tag{3.21}$$

$$\eta = \exp(-2mh/kT), \tag{3.22}$$

$$\mu = \epsilon\eta^{-1}, \tag{3.23}$$

and

$$\nu = \epsilon\eta. \tag{3.24}$$

Here, H represents a uniform magnetic field, while h represents the staggered field. The susceptibility per spin is then obtained using the relation

$$\chi_h = kT(\partial^2 \ln\Lambda/\partial h^2)\,|_{h=0}$$

$$= \frac{4m^2}{kT}\left(\eta\frac{\partial \ln\Lambda}{\partial\eta} + \eta^2\frac{\partial^2 \ln\Lambda}{\partial\eta^2}\right)\Bigg|_{\eta=1}$$

$$= \frac{4m^2}{kT}\left\{\frac{2\epsilon}{(1+\epsilon)^2}\right.$$

$$\left. + \sum_\lambda \frac{(u-1)^\lambda}{\lambda!}\sum_{i=1}^{\lambda}\sum_{j=0}^{i}\frac{b_{i-j,j}{}^\lambda[(i-2j)^2(1+\epsilon)^2 - 2\lambda\epsilon]}{(1+\epsilon)^{2\lambda+2}}\right\}, \tag{3.25}$$

where

$$b_{i-j,j}{}^\lambda = a_{i-j,j}{}^\lambda(\epsilon^i + \epsilon^{2\lambda-i}). \tag{3.26}$$

In the form of Eq. (3.25), χ_h cannot be subjected easily to Padé analysis. This is because of the existence of the two independent variables u and ϵ. Hence, two means were used to re-express the series in terms of one variable. In type-I series, the variable H was expressed as

$$H = cJ/m \tag{3.27}$$

and the series was constructed in powers of the variable

$$x = J/kT, \tag{3.28}$$

for constant values of c. In type-II series, ϵ was held constant and the series variable was $(u-1)$. Padé approximants, $[n, n]$, $n=1$, to 5, as well as $[5, 4]$ and $[4, 5]$, in the notation of Baker,[10] were fitted to both types of series expansions of $d\ln\chi_h/dx$. The critical temperatures so obtained for $H=0$, $T_c(0)$, showed good convergence to those obtained by Baker.[10]

The tendency of $T_c(H)$ to go to zero for increasing H leads to a basic problem associated with the use of high-temperature expansions for the solution of this problem. The high-temperature expansion is a power series in the variables x or $u-1$. As H increases, the susceptibility singularity moves towards larger values of x and $u-1$. Thus, we may expect a finite number of terms in the small x or $(u-1)$ expansions to contain a decreasing amount of information about the position of the singularity, with increasing H. As a result, the successive approximants show a decreasing rate of convergence with increasing H.

For some reason which is unknown to us, the x expansion shows better convergence for the square and bcc lattices, while the $(u-1)$ expansion is better for the simple cubic. For each of the lattices, there is a value of H/H_c beyond which no convergence is observed. For larger values of H, there is either no convergence, or there are no singularities in the expected region. In all cases, $T_c(H)$ has been taken as the average of the values obtained from the $[5, 5]$ and $[5, 4]$ approximants, since these might form upper

and lower bounds to the true $T_c(H)$.[20] As discussed previously,[11] over the entire region in which the results are judged to be fairly reliable, they are well fit by expressions of the form

$$T_c(H)/T_c(0)=[1-(H/H_c)^2]^{\xi} \qquad (3.29)$$

with $\xi=0.87$ and 0.36 for the two- and three-dimensional lattices, respectively. The ranges of reliability are summarized by

$$\begin{aligned} |H/H_c| &\leq 0.7 \quad \text{square and simple cubic} \\ &\leq 0.9 \quad \text{body-centered cubic.} \end{aligned} \qquad (3.30)$$

D. Calculation of the Magnetizations at the Critical Temperatures

As indicated in Eq. (2.8), the deviation from AB-type stoichometry is obtained from a knowledge of the magnetization. Thus, it was necessary to calculate the magnetization per spin at the critical temperature associated with each value of H, with $h=0$. Using Eq. (3.9) and setting $m_\alpha=m_\beta=1$, we have

$$M=-(\partial F/\partial H)_{T,h=0}$$

or

$$M=1+(kT/2)(\partial \ln\Lambda/\partial H)_{T,h=0}. \qquad (3.31)$$

Substituting Eqs. (3.13), (3.14), and (3.21) into Eq. (3.31) and performing the required differentiation yields the expression

$$M=\frac{(1-\epsilon)}{(1+\epsilon)}-m\sum_{\lambda}\frac{(u-1)^\lambda}{\lambda!}\sum_{i=1}^{\lambda}c_i^\lambda\left\{\frac{[i\epsilon^i+(2\lambda-1)\epsilon^{2\lambda-i}]}{(1+\epsilon)^{2\lambda}}-\frac{2\lambda\epsilon(\epsilon^i+\epsilon^{2\lambda-i})}{(1+\epsilon)^{2\lambda+1}}\right\}, \qquad (3.32)$$

where

$$c_i^\lambda=\sum_{j=0}^{i}a_{i-j,j}^\lambda. \qquad (3.33)$$

As in the efforts to locate T_c, it is necessary to evaluate a physical property of the system at T_c with a finite number of terms of the high-temperature series expansion. As before, Padé approximants have been used to continue the series into the region of interest. Again there is the difficulty of having the two independent variables u and ϵ. In this calculation, fixed ratios of H to T, defined by the value of T_c for given H, were used. This choice makes ϵ a constant and implies that the right-hand side of Eq. (3.32) is a power series in the variable $(u-1)$. Padé approximants of the form $[n, n]$, as well as $[5, 4]$ and $[4, 5]$, to the magnetization of Eq. (3.32) were constructed and evaluated at the values $(u-1)$ corresponding to the critical temperature for each value of H. The results are shown in Fig. 1.

[20] G. A. Baker, Advan. Theoret. Phys. **1**, 1 (1965).

In this portion of the calculation, the convergence of successive approximants to the final value was extremely rapid. On the simple cubic and square lattices, however, it was possible to obtain values only for $H/H_c\leq 0.40$ and 0.55, respectively. This limitation was imposed by the size of a number which our computer could accommodate. The nonlinear behavior of M for the square lattice is not understood. Attempts were made to determine the sensitivity of this calculation to the estimated uncertainties in $T_c(H)$. This was done by keeping the ratio of the magnetic field to the ordering energy constant, and varying T_c in calculations of the magnetization. In particular, for each value of H, the magnetization was evaluated for the individual T_c's obtained from the $[5, 5]$ and $[5, 4]$ approximants. The resulting M's differed by approximately 0.03% of their average at $H/H_c=0.2$. This difference increased smoothly to 0.2% at $H/H_c=0.7$. These uncertainties are too small to show on Fig. 1. Thus it is believed that the major uncertainties in the work presented below come from the uncertainties in the calculation of T_c versus H.

IV. T_c VERSUS COMPOSITION

A. Numerical Results

Using Eq. (2.8), the magnetization versus field relations can be converted to composition versus H. These can be combined with the calculation of T_c versus H to yield T_c versus composition, c. The results are presented in Fig. 2. The error bars indicate the uncertainty in

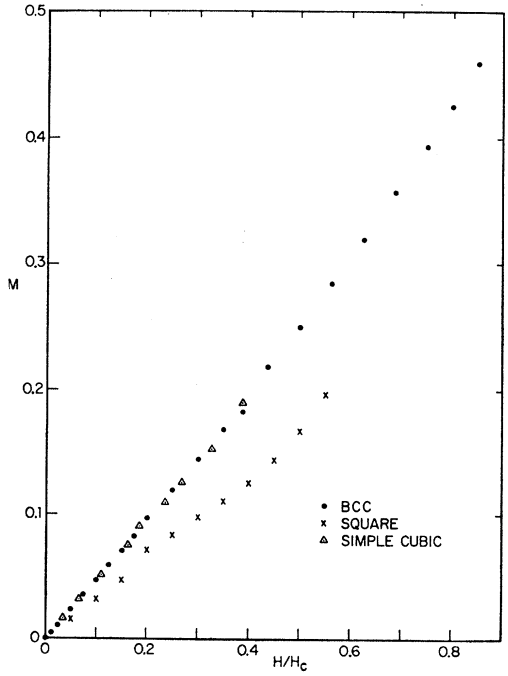

FIG. 1. Magnetization per spin at T_c as a function of applied magnetic field, H. Here, $m_\alpha=m_\beta=1$.

$T_c(c)/T_c(0.5)$ obtained from the difference in T_c's obtained from the [5, 5] and [5, 4] approximants. This uncertainty is 2.3% at $c=0.30$ and reduces smoothly to 0.13% at $c=0.41$ and 0.06% at $c=0.47$. In order to describe the results for the bcc lattice with an analytic form, we have fit them to an expression of the type

$$T_c(\delta)/T_c(0)=(1-p\delta^2)^q, \tag{4.1}$$

where

$$\delta=|N-2N_A|/2N. \tag{4.2}$$

The values obtained from a least-squares fit to $\ln[T_c(\delta)/T_c(0)]$ are $p=9.007$, and $q=0.739$. This expression fits the calculated points quite well. It should be noted, nevertheless, that there is no theoretical justification for the use of an expression of this form. In addition, it does not fit the results for the simple cubic and square lattices. It should be regarded as nothing more than a convenient means of expressing the results with a two parameter expression.

B. Beta-Brass

Sykes and Wilkinson's[21] measurements of T_c versus composition are presented in Table I. In order to compare these experimental results with the calculation presented here, it would be best to know T_c for an alloy containing 50-at.% Zn. Unfortunately, pure β brass does not exist at this composition. Indeed, Sykes and Wilkinson indicate that even their sample

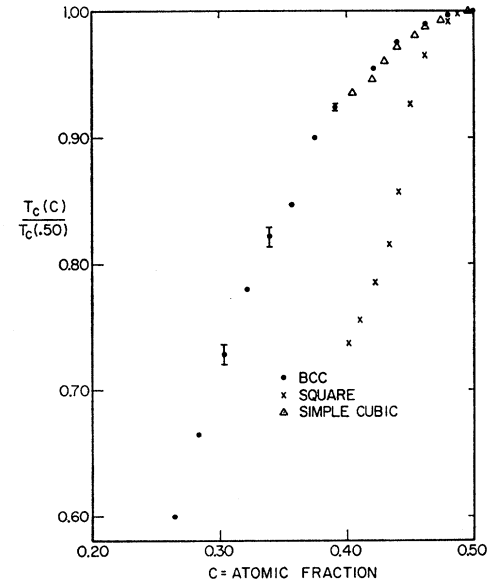

FIG. 2. Variation of the order-disorder critical temperature with binary alloy composition for the square, simple cubic, and body-centered cubic lattices. Error bars show the [5, 5] and [5, 4] approximant values for $T_c(c)/T_c(0.5)$, whose average was used for $T_c(c)/T_c(0.5)$. The accompanying composition changes are at most 0.1% at $c=0.30$.

[21] C. Sykes and H. Wilkinson, J. Inst. Metals **61**, 223 (1937).

TABLE I. Measured and corrected critical temperatures T_c of β brass at various compositions and zero pressure. ΔT_c is our estimate of the shift in T_c which would result if the lattice parameter of each sample were equal to that of the 0.490-at.% Zn sample at its T_c.

At.% Zn	T_c°K[a]	T_c/742.8°K	ΔT_c°K	$(T_c+\Delta T_c)$/742.8°K
0.442	727.7	0.9797	−11.6	0.9640
0.451	730.7	0.9837	− 9.6	0.9708
0.466	740.2	0.9965	− 6.1	0.9883
0.470	740.7	0.9972	− 5.1	0.9903
0.490	742.2	0.9992	0	0.9992

[a] C. Sykes and H. Wilkinson, J. Inst. Metals **61**, 223 (1937).

containing 49.0 at.% Zn showed traces of γ brass. For our purposes, however, we shall assume that the composition was sufficiently close to 49.0 at.% Zn so that we may use the measured T_c of that sample to determine a T_c at 50 at.% Zn of 742.8°K. The resulting values of T_c (comp)/T_c (50%) are plotted on Fig. 3. Figure 3 also shows the curve of Eq. (4.1) with the p and q values appropriate for the body-centered cubic lattice. The agreement is remarkably good. One could improve the agreement considerably by matching the point at 47 at.% Zn and arguing that the sample of 49 at.% Zn consisted of β brass with less than 49 at.% Zn and γ brass with more than 49 at.% Zn. This entire agreement is, however, illusory.

The basic assumption of this calculation is that the ordering energy, V of Eq. (2.5), is independent of composition. While there is no direct information indicating that V is a function of composition, Yoon and Bienenstock's[22] measurements indicate a strong volume dependence of T_c. This implies that any comparison between this calculation and experimental measurements must take into account the dependence of lattice parameter on composition which is indicated in the work of Beck and Smith.[23] We now proceed to do this.

Beck and Smith's measurements indicate that, at 29.8°C, the lattice parameter can be approximated quite well by the expression:

$$a=(2.8648+0.1869C)\ \text{Å}, \tag{4.3}$$

where C is the atomic fraction of Zn.

The work of Owen and Pickup[24] indicates that, except in the region of T_c, the thermal expansion coefficient is independent of composition. Since the bulk of the actual change of lattice parameter between 29.8°C and T_c occurs over the region in which the thermal expansion coefficient is independent of composition, the small variations of it and T_c itself may be neglected. Thus the lattice parameter at T_c is well approximated by the expression

$$a=(2.8748+0.1869C)\ \text{Å} \tag{4.4}$$

[22] D. N. Yoon and A. Bienenstock (to be published).
[23] L. H. Beck and C. S. Smith, J. Inst. Metals **4**, 1079 (1952).
[24] E. A. Owen and L. Pickup, Proc. Roy. Soc. (London) **A145**, 258 (1934).

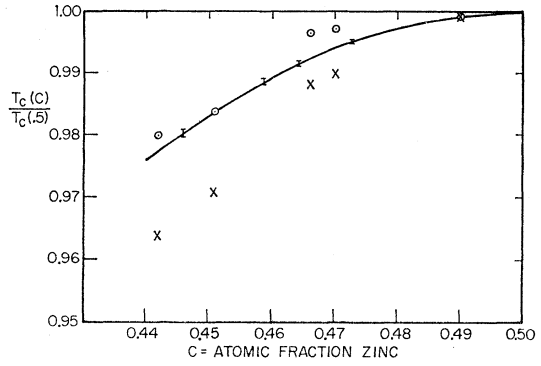

FIG. 3. Comparison of the calculated values of the composition dependence of T_c (solid curve) with experimentally observed values for β brass at atmospheric pressure (shown as circles). The crosses indicate our estimates of the critical temperatures at a fixed lattice constant corresponding to that of β brass containing 49 at.% zinc at its critical temperature and atmospheric pressure.

obtained by using the total change in lattice parameter at one composition.

Yoon and Bienenstock's measurements indicate a pressure dependence of T_c given by

$$dT_c/dP=(-0.078+3.200C)\,^\circ\mathrm{K/kbar}. \quad (4.5)$$

McManus[25] finds a compressibility of 10.5×10^{-4}/kbar for a sample of β brass at T_c. He also finds that the compressibility of β brass varies by less than 3% over the pure β-brass range of the Cu-Zn phase diagram at room temperature. Thus, we use his value at T_c for all compositions.

These data can be used to calculate T_c for each composition at the lattice constant of the 49% Zn at its T_c. To each T_c must be added

$$\Delta T_c=\left(\frac{\partial T_c}{\partial P}\right)\left[\frac{-1}{3V}\left(\frac{\partial V}{\partial P}\right)_T\right]^{-1}\frac{\Delta a}{a}, \quad (4.6)$$

where Δa is the lattice constant at composition C minus that at $C=0.49$. That is

$$\Delta a=0.1869C-0.0916. \quad (4.7)$$

Substitution of Eqs. (4.5) and (4.7) as well as McManus' value of the compressibility into Eq. (4.6) yields the expression

$$\Delta T_c=\frac{(7.20-305.9C+594.4C^2)\,^\circ\mathrm{K}}{(1+0.0650C)}. \quad (4.8)$$

The calculated ΔT_c are listed in Table I and the revised values of T_c (comp.)/742.8°K are shown as the crosses in Fig. 3. It is seen that this adjustment to constant interatomic distance completely destroys the agreement between the calculation and the experimental measurements.

These results leave the following possibilities open:

(1) The corrections applied to convert the results to constant lattice parameter are inaccurate.

(2) This calculation does not represent the Ising model to a sufficient degree of accuracy.

(3) A single volume-dependent nearest-neighbor ordering energy is insufficient to describe the order-disorder transformation of β brass over the composition range in which it is observed.

The first of these possibilities seems highly unlikely. It is true that it has been necessary to approximate both the lattice parameters and the compressibilities of the alloys. Since the compressibility does not vary by more than 3% over the composition range at room temperature, it seems doubtful that the variation is significantly greater than this at T_c. Similarly, it is doubtful that the lattice parameter expression used is significantly in error. Nevertheless, the picture does not improve if we assume that there is an error as large as, say, 15% in the correction to T_c. For instance, if it is assumed that the correction to the data at $C=0.422$ should be 15% less than that used, the resulting $T_c(C)/T_c(0.5)$ is only increased to 0.9663. This improvement is still quite insufficient to bring agreement between theory and experiment. Thus, we feel that the first possibility is not the cause of the disagreement.

The second possibility is that the Padé approximants to the high-temperature series expansions do not represent adequately the properties of the Ising model. This possibility is, of course, always open. There is some indication that this is not the case here. First of all, the compositions considered here correspond to rather small departures from the T_c associated with zero-magnetic field. The convergence of the approximants is quite good for the determination of the T_c's. The problems associated with the small values of the critical temperatures appear only at much larger deviations from stoichiometry. This, however, only means that the approximant scheme is consistent. The work of Huiskamp[26] indicates that the calculations[11] of T_c versus H for the Ising antiferromagnet, which form part of the basis of this work, are in good agreement with experimental measurements on two Ising-like systems. While there is no analagous data for the magnetization at T_c, this property should be well represented by the approximants, since it is a slowly varying function at T_c. Indeed, the convergence of the approximants is extremely rapid in the T_c region of interest. Thus, although it is not possible for us to evaluate the order of magnitude of the approximations associated with the use of the approximants, it appears as if they are not likely to have caused the disagreement observed.

The third conclusion has already been reached independently by Yoon and Bienenstock[22] on the basis of

[25] G. M. McManus, Phys. Rev. **129**, 2004 (1963).

[26] W. J. Huiskamp, Ann. Acad. Sci. Fennicae **6**, 180 (1966).

their measurements of the pressure dependence of T_c as a function of concentration. Thus, this work forms additional evidence for their conclusion. Since these authors are preparing a manuscript describing studies of the cause of the breakdown of the model, we shall not discuss this matter further.

ACKNOWLEDGMENTS

One of us (AB) is deeply indebted to W. Marshall for suggesting this problem and to J. Hubbard as well for many helpful discussions during the period when AB was at the Atomic Energy Research Establishment, Harwell, England. In addition, the group at King's College, London, under the direction of Professor C. Domb, helped AB in every portion of the work. M. F. Sykes suggested the techniques which allowed the authors to derive the high-temperature expansions, obtained, with his co-workers, the necessary low-temperature expansions, and made many other significant contributions. M. E. Fisher frequently made helpful suggestions. L. Morgan, of AERE, Harwell, helped considerably with the early stages of computer programming.

APPENDIX A. TABULATION OF THE $a_{j,k}{}^{\lambda}$

This Appendix contains a tabulation (Table II) of the $a_{j,k}{}^{\lambda}$ of Eq. (3.19) for the body-centered cubic, simple cubic, and square lattices. Those coefficients which can be obtained from the relation $a_{j,k}{}^{\lambda}=a_{k,j}{}^{\lambda}$ are not included.

TABLE II. The $a_{j,k}$ of Eq. (3.19).

λ	j	k	$a_{j,k}{}^{\lambda}$ body-centered cubic	simple cubic	square
1	1	0	2	2	1
2	1	0	12	6	2
2	2	0	−2	−2	−1
2	1	1	−32	−18	−8
3	1	0	24	6	0
3	2	0	−96	−42	−12
3	1	1	−864	−324	−72
3	3	0	4	3	2
3	2	1	540	225	66
4	1	0	24	0	0
4	2	0	−744	−180	−12
4	1	1	−6528	−1440	−96
4	3	0	744	288	72
4	2	1	32208	9144	1392
4	4	0	−12	−9	−6
4	3	1	−8352	−2736	−576
4	2	2	−41760	−12132	−2040
5	1	0	0	0	0
5	2	0	−3360	−360	0
5	1	1	−33600	−3600	0
5	3	0	14880	3240	240
5	2	1	5 35200	93600	5280
5	4	0	−6240	−2160	−480
5	3	1	−9 42240	−2 08800	−22800
5	2	2	−37 19040	−7 50240	−68640
5	5	0	48	36	24
5	4	1	1 26000	33660	5400
5	3	2	21 52320	4 60800	49200
6	1	0	0	0	0
6	2	0	−10080	−360	0
6	1	1	−1 20960	−4320	0
6	3	0	1 61280	18000	240
6	2	1	61 08480	5 91840	7200
6	4	0	−2 62080	−50760	−3600
6	3	1	−286 67520	−39 78720	−1 74240
6	2	2	−1024 01280	−131 99760	−5 05440
6	5	0	57600	18000	3600
6	4	1	246 41280	43 71840	3 56400
6	3	2	2829 80160	421 35840	24 71760
6	6	0	−240	−180	−120
6	5	1	−19 26720	−4 29840	−54720
6	4	2	−904 15440	−147 61980	−10 68120
6	3	3	−2825 46240	−426 78720	−26 49120
7	1	0	0	0	0
7	2	0	−20160	0	0
7	1	1	−2 82240	0	0
7	3	0	11 89440	60480	0

TABLE II. (*Continued*)

λ	j	k	$a_{j,k}^{\lambda}$ body-centered cubic	simple cubic	square
7	2	1	520 73280	24 34320	0
7	4	0	−55 23840	−5 74560	−10080
7	3	1	−5869 18080	−473 10480	−6 04800
7	2	2	−20142 66240	−1534 68000	−17 94240
7	5	0	44 75520	7 71120	50400
7	4	1	12429 84960	1385 44560	46 87200
7	3	2	1 18250 09280	11437 97760	297 36000
7	6	0	−5 84640	−1 66320	−30240
7	5	1	−6124 60800	−887 24160	−55 74240
7	4	2	−1 71364 23360	−19356 32160	−764 76960
7	3	3	−4 72463 30880	−49917 47040	−1726 09920
7	7	0	1440	1080	720
7	6	1	304 31520	57 68280	5 99760
7	5	2	33862 04640	4323 03480	222 11280
7	4	3	2 64217 06080	29209 49640	1132 63920
8	1	0	0	0	0
8	2	0	−20160	0	0
8	1	1	−3 22560	0	0
8	3	0	64 91520	1 20960	0
8	2	1	3407 84640	61 68960	0
8	4	0	−770 71680	−40 21920	−10080
8	3	1	−89710 38720	−3851 36640	−8 06400
8	2	2	−3 05090 15040	−12596 77440	−25 80480
8	5	0	1631 34720	153 61920	2 82240
8	4	1	4 10668 87680	27162 77760	303 60960
8	3	2	35 66599 14240	2 10429 27360	1921 65120
8	6	0	−770 71680	−118 54080	−7 05600
8	5	1	−4 79630 59200	−43477 86240	−1148 31360
8	4	2	−103 27550 28480	−7 62879 60000	−13751 13600
8	3	3	−264 97258 90560	−18 48292 99200	−29733 58080
8	7	0	64 91520	16 93440	2 82240
8	6	1	1 49506 56000	17961 35040	891 87840
8	5	2	90 27231 89760	7 90246 19520	21864 72960
8	4	3	568 92783 62880	43 99877 66400	95138 26560
8	8	0	−10080	−7560	−5040
8	7	1	−5009 35680	−817 68960	−70 96320
8	6	2	−11 87310 29760	−1 20851 13600	−4568 25600
8	5	3	−201 45875 09760	−16 72003 46880	−42571 46880
8	4	4	−488 18827 81440	−38 21850 04320	−86448 70080
9	1	0	0	0	0
9	2	0	0	0	0
9	1	1	0	0	0
9	3	0	266 11200	1 20960	0
9	2	1	16982 78400	76 20480	0
9	4	0	−7983 36000	−188 69760	0
9	3	1	−10 77710 05440	−22055 84640	0
9	2	2	−36 97805 26080	−74158 15680	0
9	5	0	38073 36960	1879 71840	7 25760
9	4	1	99 92147 55840	3 68199 82080	979 77600
9	3	2	834 65215 94880	28 13513 87520	6560 87040
9	6	0	−44958 41280	−3796 93440	−67 73760
9	5	1	−239 25476 73600	−12 99444 24960	−12091 16160
9	4	2	−4483 18586 41920	−205 48613 43360	−1 40209 57440
9	3	3	−11029 55964 36480	−481 49603 71200	−2 98882 48320
9	7	0	13629 77280	1879 71840	101 60640
9	6	1	173 22091 31520	12 91787 48160	26998 27200
9	5	2	7570 35291 80160	433 85689 67040	5 55184 62720
9	4	3	41953 92209 97120	2159 12235 57120	22 29723 41760
9	8	0	−783 82080	−188 69760	−29 03040
9	7	1	−36 52474 29120	−3 68559 07200	−14761 95840
9	6	2	−4350 89665 38240	−300 34478 07360	−6 00522 85440
9	5	3	−55651 75667 25120	−3221 95541 87520	−45 50950 65600
9	4	4	−1 24610 32526 74560	−6849 30498 73920	−86 98654 54080
9	9	0	80640	60480	40320
9	8	1	86285 60640	12263 52960	903 57120
9	7	2	401 37503 61600	33 08616 46080	94624 58880
9	6	3	13442 44151 57760	854 41830 56640	14 84341 28640
9	5	4	68131 10755 58400	3884 78839 79520	54 18763 66080
10	1	0	0	0	0
10	2	0	0	0	0
10	1	1	0	0	0
10	3	0	798 33600	0	0
10	2	1	61689 60000	0	0

TABLE II. (*Continued*)

λ	j	k	$a_{j,k}^{\lambda}$ body-centered cubic	simple cubic	square
10	4	0	−64665 21600	−598 75000	0
10	3	1	−104 17704 19200	−87091 20000	0
10	2	2	−364 65230 59200	−3 04710 33600	0
10	5	0	6 50324 50560	15807 05280	7 25760
10	4	1	1908 08110 08000	36 36493 05600	1270 08000
10	3	2	15814 42579 58400	282 71436 48000	9434 88000
10	6	0	−16 26210 43200	−73646 49600	−326 59200
10	5	1	−8640 56325 88800	−267 81850 36800	−69818 11200
10	4	2	−1 50787 20198 52800	−4066 88688 00000	−8 36075 52000
10	3	3	−3 62235 73413 88800	−9380 76515 71200	−17 90885 37600
10	7	0	12 03092 35200	90901 44000	1524 09600
10	6	1	12445 52843 52000	557 77014 72000	4 25839 68000
10	5	2	4 53684 30936 19200	16283 28925 44000	82 44887 61600
10	4	3	23 21801 29714 17600	75914 32472 06400	319 80940 99200
10	8	0	−2 49734 01600	−31026 24000	−1524 09600
10	7	1	−6031 37767 68000	−373 82808 96000	−6 26621 18400
10	6	2	−4 93840 20954 24000	−22264 10323 20000	−206 80785 21600
10	5	3	−53 00494 87080 96000	−2 04901 47804 67200	−1401 91502 97600
10	4	4	−112 71956 15927 80800	−4 16029 97036 16000	−2588 48182 65600
10	9	0	10233 21600	2286 14400	326 59200
10	8	1	903 14517 88800	77 36964 48000	2 54197 44000
10	7	2	1 98004 70922 62400	10934 52550 84800	162 12534 91200
10	6	3	47 24498 09147 90400	2 08464 67950 33600	1991 30944 32000
10	5	4	208 74361 04667 64800	8 35988 16643 77600	6550 34107 39200
10	10	0	−7 25760	−5 44320	−3 62880
10	9	1	−15 57480 96000	−1 94539 96800	−12337 92000
10	8	2	−13328 29536 19200	−901 41433 20000	−19 95204 96000
10	7	3	−8 19071 55832 32000	−40529 37047 04000	−495 54820 22400
10	6	4	−78 72166 51070 97600	−3 33840 16076 54400	−2993 73205 82400
10	5	5	−162 42956 92167 32160	−6 57327 85764 71040	−5351 40108 51840
11	1	0	0	0	0
11	2	0	0	0	0
11	1	1	0	0	0
11	3	0	1596 67200	0	0
11	2	1	1 46893 82400	0	0
11	4	0	−4 18328 06400	−1197 50400	0
11	3	1	−814 76575 48800	−2 17945 72800	0
11	2	2	−2928 51998 20800	−7 97537 66400	0
11	5	0	87 01862 40000	95800 32000	0
11	4	1	29643 84428 54400	266 61229 05600	0
11	3	2	2 48688 67339 00800	2152 86071 61600	0
11	6	0	−422 76681 21600	−9 84348 28800	−798 33600
11	5	1	−2 42791 12585 72800	−4062 54429 50400	−2 12357 37600
11	4	2	−41 12133 86174 97600	−61627 35192 76800	−27 51065 85600
11	3	3	−97 59823 46228 73600	−1 41565 85726 97600	−60 13066 75200
11	7	0	639 37133 56800	26 20138 75200	11975 04000
11	6	1	6 36084 58636 80000	16489 12712 83200	38 59954 56000
11	5	2	209 47849 71890 68800	4 50371 91386 88000	754 10818 56000
11	4	3	1020 65341 84906 75200	20 25582 53059 00800	2910 28598 78400
11	8	0	−319 62180 09600	−21 61494 72000	−33530 11200
11	7	1	−6 02231 85082 36800	−22408 67680 12800	−140 06805 12000
11	6	2	−396 30820 09361 40800	−11 23903 97913 02400	−4244 95209 60000
11	5	3	−3799 90271 60252 92800	−94 16911 86108 28800	−27228 06358 27200
11	4	4	−7807 19271 01217 28000	−185 67757 15812 86400	−49362 58381 82400
11	9	0	47 61275 90400	5 35284 28800	23950 08000
11	8	1	2 06263 94874 62400	10722 10353 98400	145 95178 75200
11	7	2	297 37248 63943 68000	10 67498 22364 41600	7343 11847 80800
11	6	3	5722 40189 90476 80000	168 67434 16157 18400	78568 29332 35200
11	5	4	23058 82899 02057 47200	623 05150 77154 36800	2 42733 59776 51200
11	10	0	−1 43700 48000	−29937 60000	−3991 68000
11	9	1	−22760 54339 32800	−1670 67375 55200	−45 66481 92000
11	8	2	−86 87518 10631 93600	−3 88510 49780 92800	−4364 76636 28800
11	7	3	−3627 34833 49931 52000	−123 82078 73474 88000	−82306 58147 71200
11	6	4	−29013 77101 36361 47200	−862 78289 98041 79200	−4 33180 00357 63200
11	5	5	−56677 95163 40083 20000	−1615 26512 30550 91200	−7 42304 37270 52800
11	11	0	72 57600	54 43200	36 28800
11	10	1	294 62590 08000	32 60204 64000	1 80024 76800
11	9	2	4 40134 30048 89600	24693 80782 17600	431 04954 81600
11	8	3	468 59532 25726 08000	18 30235 15803 74400	16160 75157 31200
11	7	4	7953 24819 60594 43200	255 12157 13530 17600	1 52080 43735 80800
11	6	5	30519 07817 56439 04000	896 83292 18173 24800	4 46171 65262 20800