[13]P. G. de Gennes, Phys. Lett. A 30, 454 (1969); R. G. Priest, Phys. Rev. Lett. 26, 423 (1971).

[14]J. Kanamori, J. Appl. Phys. 31, 145 (1960); R. J. Elliott, A. P. Young, and S. R. P. Smith, J. Phys. C 4, L317 (1971); R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. Soc. Lond. A 328, 217 (1972).

[15]H. H. Chen and P. M. Levy, Phys. Rev. Lett. 27, 1383 (1971). In this letter the sign of the energy correction term $\langle H \rangle /2$ in Eq. (3) is incorrect. It should be $-\langle H \rangle /2$.

[16]U. Fano, Spectroscopic and Group Theoretical Method in Physics, edited by F. Bloch et al. (North-Holland, Amsterdam, 1968), p. 153. In this reference Eq. (20), which is similar to our Eq. (8), is given as (in our notation) (A) $\{(1-\langle Q_2 \rangle)\langle S_x \rangle^2 + (1+\langle Q_2 \rangle)\langle S_y \rangle^2 + (1-\langle Q_0 \rangle)\langle S_z \rangle^2\} \leq (1-\langle Q_0 \rangle) \ [(1/3)\langle Q_0 \rangle+2/3]^2 -\langle Q_2 \rangle^2.$ Following the method outlined in the paper we find that this equation should read
(B)$\{[1+(1/2)\langle Q_0 \rangle - (3/2)\langle Q_2 \rangle]\langle S_x \rangle^2 + [1+(1/2)\langle Q_0 \rangle +(3/2)\langle Q_2 \rangle]\langle S_y \rangle^2 + (1-\langle Q_0 \rangle)\langle S_z \rangle^2\} \leq (1-\langle Q_0 \rangle)\{[(1/3)\langle Q_0 \rangle+2/3]^2 -\langle Q_2 \rangle^2\}.$ Equation (B) is the same as our Eq. (8).

[17]L. D. Landau and E. M. Lifshitz, Statistical Physics (Pergamon, London, 1958), pp. 434ff.

[18]S. Strässler and C. Kittel, Phys. Rev. 139, A758 (1965).

[19]We take this opportunity to point out an error in our letter, Ref. 15. We neglected the possibility of ordering along the [111] direction and reached the erroneous conclusion in Ref. 15 that a one-sublattice system with cubic symmetric Hamiltonian will have two phase transitions. As shown in Sec. III C we find that a system with cubic symmetry orders along the [111] direction and has one phase transition for that range of interaction constants in which we originally thought two transitions occured. If we let $I_x = I_y = I_z = I\alpha$, $I_{xy} = I_{22} = I\beta$, and $I_{yz} = I_{xz} = 0$, then Fig. 1(c) in Ref. 15 is in fact the phase diagram for an axially symmetric Hamiltonian, Eq. (27), for $\alpha,\beta \gg 1$.

[20]For $\alpha,\beta \gg 1$ and for dipolar ordering along the [110] direction instead of along the x axis, our Hamiltonian, Eq. (27) reduces to the one studied by Allen in Ref. 8, Eq. (10).

[21]By parallel dipole and quadrupole moments we mean that the quadrupoles have a unique symmetry axis which is parallel to the dipole moments.

High-Temperature Series Expansions for a Spin-1 Model of Ferromagnetism[*]

H. H. Chen[†]

Institute of Physics, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

Peter M. Levy

Department of Physics, New York University, New York, New York 10003

(Received 30 October 1972)

High-temperature series expansions are derived up to terms in T^{-4} for the dipole and quadrupole susceptibilities for arbitrary lattices. The expansions are evaluated for a spin-1 isotropic Hamiltonian with bilinear and biquadratic pair interactions. We compare the dipole and quadrupole phase transition temperatures determined from these series to those obtained by the molecular-field and constant-coupling approximations. There are large uncertainties in the estimates of the quadrupole transition temperatures because of the few terms in the series.

The Hamiltonian for a magnetic system with isotropic bilinear and biquadratic pair interactions between nearest-neighbor ions on an arbitrary lattice is given by

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} [\vec{S}_i \cdot \vec{S}_j + \alpha(\vec{S}_i \cdot \vec{S}_j)^2]. \tag{1}$$

This system has been investigated mostly for spin-1, $S = 1$, and when α is either very small or $\alpha = 1$. Recently, this Hamiltonian has been studied for $S = 1$ and for all values of α by using the molecular-field[1,2] and constant-coupling[3] approximations. It is generally felt that effective-field theories give only qualitative results and do not accurately predict the critical temperatures. We report in this paper on a study of the critical temperatures of the spin-1 Hamiltonian found by deriving and analyzing the high-temperature series expansions for the dipole and quadrupole susceptibilities.

For $\alpha \ll 1$ and for arbitrary spin the high-temperature series expansions for the dipole suscepti-

bility have been calculated up to the term T^{-4} by Joseph[4] by using a diagrammatic method. For $\alpha = 1$ and $S = 1$ the dipole susceptibility series expansions for terms through T^{-7} was obtained by Allan and Betts[5] by using a cluster-expansion method together with group-theoretical techniques. Here we calculate the dipole and the quadrupole susceptibility series to terms through T^{-4} for $S = 1$ and for arbitrary α by using the cluster-expansion method.[6] The estimates of the critical temperatures we obtain particularly those from the quadrupole series have large uncertainties because of the few terms in the series.

The zero-field dipole susceptibility χ_1 is proportional to the mean square fluctuation of the dipole moment $S_z = \sum_i S_{iz}$, i.e.,

$$\chi_1 = C_1 \beta \Delta(S_z), \tag{2}$$

where

$$\Delta(S_z) = \langle S_z^2 \rangle - \langle S_z \rangle^2$$

and

$$\langle S_z^2 \rangle = \text{Tr} \, S_z^2 e^{-\beta \mathcal{K}} / \text{Tr} \, e^{-\beta \mathcal{K}}.$$

β is the inverse temperature, $(k_B T)^{-1}$, and C_1 is a constant. For a spin-1 system besides the dipole moments S_x, S_y, and S_z, there are five additional ordering parameters, the quadrupole moments $O_0^{[2]}$, $O_2^{[2]}$, O_{xy}, O_{xz}, and O_{yz}.[1] Associated with each ordering parameter, a susceptibility can be defined as the thermal fluctuation of that moment. Because of the invariance of the Hamiltonian under rotations it is sufficient to investigate the quadrupole susceptibility for one of the quadrupole moments, e.g.,

$$O_0^{[2]} = \sum_i [3 S_{iz}^2 - S(S+1)].$$

The quadrupole susceptibility χ_2 is written as

$$\chi_2 = C_2 \beta \Delta(O_0^{[2]}), \tag{3}$$

where the meaning of the symbols is the same as in Eq. (2). As we approach the stability limit of the high-temperature phase either χ_1 or χ_2 diverge. If χ_1 diverges at a temperature T_c equal to or greater than the temperature T_Q at which χ_2 diverges, the system has a second-order phase transition from the paramagnetic to a ferromagnetic state. Similarly, if $T_Q > T_c$ the system undergoes a second-order phase transition to a ferroquadrupolar[1] state at T_Q. All this assumes that a first-order phase transition does not occur at a temperature higher than T_c or T_Q. We will discuss this point in greater detail further on.

Since the susceptibilities χ_1 and χ_2 are extensive thermodynamic quantities, we can derive the high-temperature series expansions by means of the cluster-expansion method.[6] This method states that the susceptibility (or other extensive quantity) per spin on the lattice G is

$$\chi(G, T) = \sum_{i=1}^{\infty} (C_i; \, G) f_i(T), \tag{4}$$

where $(C_i; \, G)$ is the high-temperature lattice constant of the cluster C_i on the lattice G. The f_i are given recursively by

$$f_i(T) = \chi(C_i, \, T) - \sum_{j=1}^{i-1} (C_j; \, C_i) f_j(T).$$

$(C_i; \, C_j)$ is the lattice constant of the cluster C_i and C_j and $\chi(C_i, \, T)$ is the susceptibility of the cluster C_i. The lattice constants $(C_i; \, C_j)$ and $(C_i; \, G)$ are known.[6] The lowest power in T^{-1} to occur in f_i is equal to or greater than the number of pair interactions in the cluster C_i.

It is convenient to reexpress the high-temperature series expansion Eq. (4) in the form

$$\chi = \frac{C}{T} \left[1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{J\beta}{3} \right)^n \sum_{m=0}^{n} a_{nm} \alpha^m \right], \tag{5}$$

where the coefficients a_{nm} contain the lattice constants $(C_i; \, C_j)$, $(C_i; \, G)$ and the susceptibilities $f_i(T)$. The constant C for the dipole susceptibility is $C = 2N/3k$; we assume that $g\mu_B = 1$. Similarly for the quadrupole susceptibility we define it as

$$C = 2N/k.$$

In order to obtain the susceptibility series to terms in T^{-4}, we have to evaluate the traces of $\mathcal{K}^n$, $\mathcal{K}^n S_z^2$, and $\mathcal{K}^n (O_0^{[2]})^2$ for $n \leq 4$ and for all clusters containing up to four pairs of interactions. To explain our method of evaluating the traces for finite clusters, let us consider a cluster of four ions. The dimension of the matrices over which traces are evaluated is $(2S+1)^4 \times (2S+1)^4$, i.e., 81×81. Although calculations (mainly multiplication) with matrices of dimension 81×81 can be handled by a fast computer, we considerably simplify matters by writing the matrices in a representation where the basis states are simultaneous eigenfunctions of S_z and $S^2 = (\sum_i \vec{S}_i)^2$. The method used to express the matrices in the S^2, S_z representation is straightforward. We first write the matrices in the representation in which the basis states are eigenstates of S_{1z}, S_{2z}, S_{3z}, and S_{4z}. The transformation matrix between the two representations is constructed by using the rules of the addition of angular momenta. Since $[\mathcal{K}, \, S_z] = [\mathcal{K}, \, S^2] = 0$, the Hamiltonian does not have matrix elements between states of different S^2 and S_z. Thus the Hamiltonian is reduced into a direct sum of submatrices associated with different sets of eigenvalues of S^2 and S_z. The matrix of $(O_0^{[2]})^2$ contains off-diagonal elements between states with different eigenvalues of S^2 and the same eigenvalue of S_z. However, these off-diagonal elements do not contribute to $\text{Tr} \, \mathcal{K}^n (O_0^{[2]})^2$ since $\mathcal{K}^n$ does not have off-diagonal elements. Therefore, the size of the largest matrix involved in the trace calculations is determined by the number of states having the same eigenvalues of S^2 and S_z. By using this method we are able to reduce the trace calculation for a four-spin cluster from 81×81 matrices to submatrices of which the largest is 6×6. These traces are then evaluated by machine calculations.

The coefficients a_{nm} for the dipole susceptibility χ_1 are given as

$$a_{10} = 2(\sigma + 1), \quad a_{11} = -(\sigma + 1),$$

$$a_{20} = (\sigma + 1)(8\sigma - 3), \quad a_{21} = -8(\sigma + 1)(\sigma - 1),$$

$$a_{22} = (\sigma + 1)(2\sigma - 7),$$

$$a_{30} = 12(\sigma + 1)(4\sigma^2 - 3\sigma - 3) - 360 p_3,$$

$$a_{31} = -3(\sigma + 1)(24\sigma^2 - 38\sigma - 3) + 270 p_3,$$

$$a_{32} = 12(\sigma + 1)(3\sigma^2 - 11\sigma + 4) - 360 p_3,$$

$$a_{33} = -3(\sigma + 1)(2\sigma^2 - 14\sigma + 11),$$

$$a_{40} = 3(\sigma+1)(128\sigma^3 - 144\sigma^2 - 124\sigma + 75)$$
$$- 360\,p_3(16\sigma+1) - 3840\,p_4,$$

$$a_{41} = -48(\sigma+1)(16\sigma^3 - 33\sigma^2 + 7\sigma + 15)$$
$$+ 2880\,p_3(5\sigma - 3) + 9600\,p_4,$$

$$a_{42} = 6(\sigma+1)(96\sigma^3 - 378\sigma^2 + 362\sigma + 165)$$
$$- 1440\,p_3(8\sigma - 9) - 7680\,p_4,$$

$$a_{43} = -24(\sigma+1)(8\sigma^3 - 54\sigma^2 + 91\sigma + 20)$$
$$+ 720\,p_3(4\sigma - 9) + 2880\,p_4,$$

$$a_{44} = 3(\sigma+1)(8\sigma^3 - 84\sigma^2 + 246\sigma + 35)$$
$$+ 360\,p_3 - 720\,p_4.$$

Here $\sigma + 1 = q$ is the coordination number of the lattice, p_3 and p_4 are the lattice constants given by Domb.[6] For $\alpha = 0$ and 1, these results reduce ex-

actly to those for the Heisenberg[7] and the exchange models,[5] respectively. For small α, by neglecting terms quadratic and higher order in α, we find our results agree to those obtained by Joseph except for the coefficient a_{41}.[8]

For the quadrupole susceptibility χ_2 the coefficients a_{nm} are as follows:

$$a_{10} = 0, \quad a_{11} = \sigma + 1, \quad a_{20} = 3(\sigma+1),$$

$$a_{21} = -12(\sigma+1), \quad a_{22} = (\sigma+1)(2\sigma+7),$$

$$a_{30} = -18(\sigma+1) + 216\,p_3,$$

$$a_{31} = -9(\sigma+1)(2\sigma - 7) - 432\,p_3,$$

$$a_{32} = -90(\sigma+1) + 216\,p_3,$$

$$a_{33} = 3(\sigma+1)(2\sigma^2 + 2\sigma + 11),$$

$$a_{40} = -27(\sigma+1)(4\sigma+3) - 1944\,p_3 + 3456\,p_4,$$
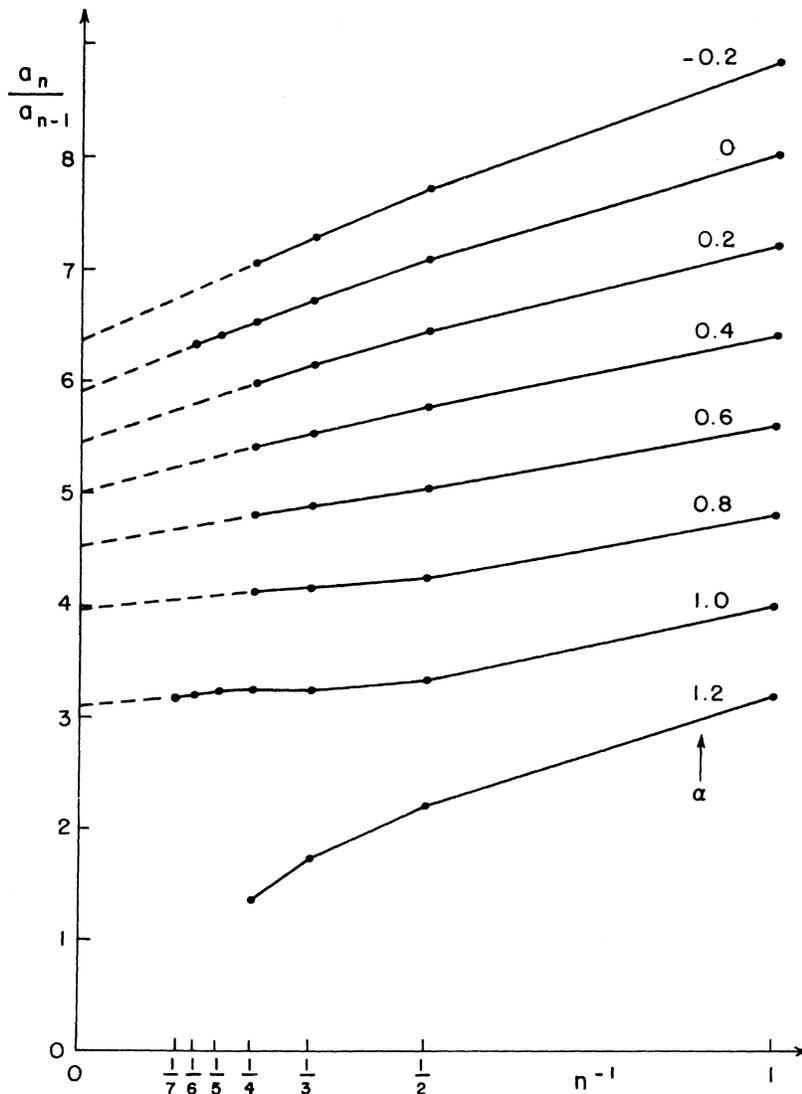
FIG. 1. Dependence upon the inverse order $1/n$ of the ratios of successive coefficients a_n/a_{n-1} in the dipolar susceptibility series for the fcc lattice. The limiting values $(n \to \infty)$ of the ratios are the critical temperatures kT_c/J. α is the ratio of biquadratic to bilinear interaction constants.

$\dfrac{a_n}{a_{n-1}}$

8

2.0

7

1.8

1.6

6

1.4

5

1.2

1.0

4

0.8

3

0.6

2

$\uparrow$
α

1

0

$\dfrac{1}{7}\ \dfrac{1}{6}\ \dfrac{1}{5}\quad \dfrac{1}{4}\qquad \dfrac{1}{3}\qquad\qquad \dfrac{1}{2}\qquad\qquad n^{-1}\qquad\qquad 1$
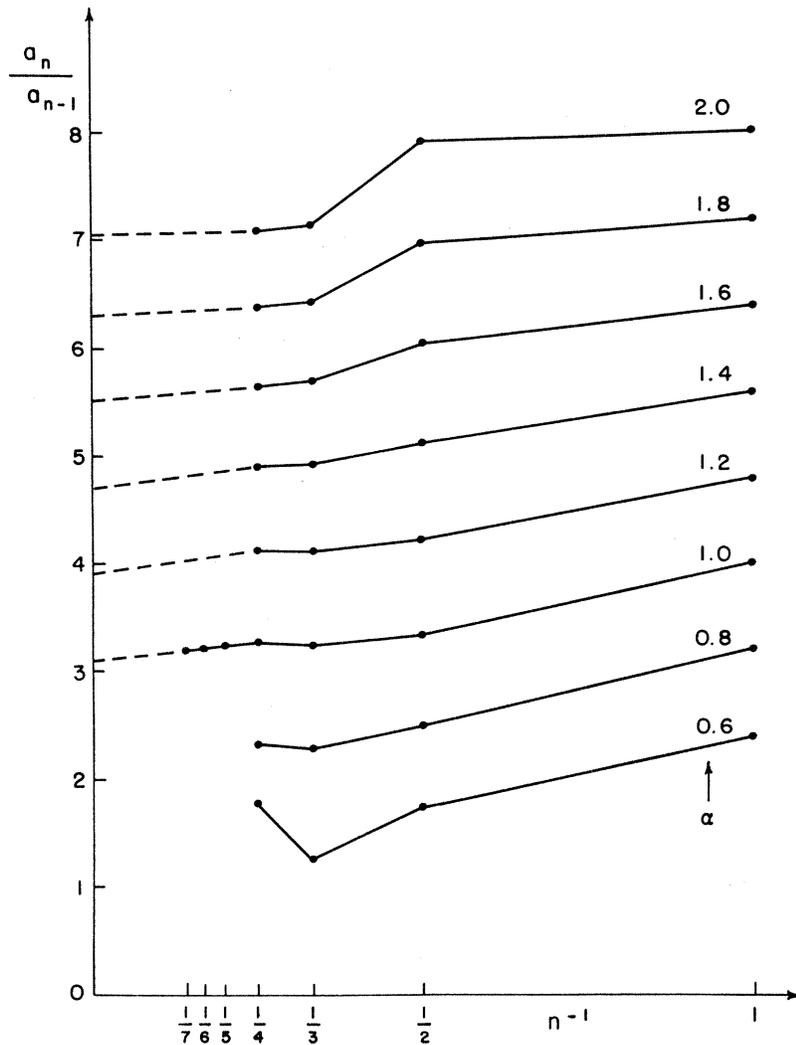
FIG. 2. Dependence upon the inverse order $1/n$ of the ratios of successive coefficients a_n/a_{n-1} in the quadrupolar susceptibility series for the fcc lattice. The limiting values of the ratios are the critical temperatures kT_Q/J. α is the ratio of biquadratic to bilinear interaction constants.

$a_{41} = 72(\sigma+1)(13\sigma+5) + 3024 p_3 - 8064 p_4,$

$a_{42} = -18(\sigma+1)(6\sigma^2+100\sigma+15) - 4104 p_3 + 6912 p_4,$

$a_{43} = 216(\sigma+1)(7\sigma+1) + 1296 p_3 - 2880 p_4,$

$a_{44} = 3(\sigma+1)(8\sigma^3+12\sigma^2 - 174\sigma - 35)$
$$- 432 p_3 + 816 p_4.$$

It has been shown by Chen and Joseph[9] that for $\alpha = 1$ and $S = 1$, the dipole and the quardupole susceptibilities are exactly the same. The present calculations agree with this result.

The above series are analyzed by standard techniques[10] to obtain the temperatures T_c and T_Q at which the dipole and the quadrupole susceptibilities diverge. In Figs. 1 and 2 we show the successive ratios a_n/a_{n-1} for the dipole and quadrupole susceptibility series for the fcc lattice and for several values of α. The extrapolated limiting values $(n \rightarrow \infty)$ of these ratios predict the critical tempera-

tures T_c and T_Q shown in Fig. 3; the error bars in Fig. 3 denote the uncertainties in the extrapolated values of the critical temperatures.

In the region $\alpha < 1$ the uncertainties in the estimates of T_c are small even though we have only five terms in the dipole series. The reasons for this are, (1) the series are very smooth for $\alpha < \frac{2}{3}$ (see Fig. 1), (2) we know the values of T_c for $\alpha = 0$ and $\alpha = 1$ from the longer series for the Heisenberg[7] and exchange[5] models, and (3) it is reasonable to assume that the critical temperature is a smooth function of the parameter α. For $\alpha > 1$ the uncertainties (error bars in Fig. 3) in our estimates of T_Q are considerably larger; the series does not rapidly converge (see Fig. 2).

We are unable to obtain values for T_c in the region $\alpha > 1$, and for T_Q in the region $\alpha < 1$ because the respective series are not well behaved in these regions. However we are sure that T_Q will not be higher than T_c for $\alpha < 1$, and T_c is lower than T_Q
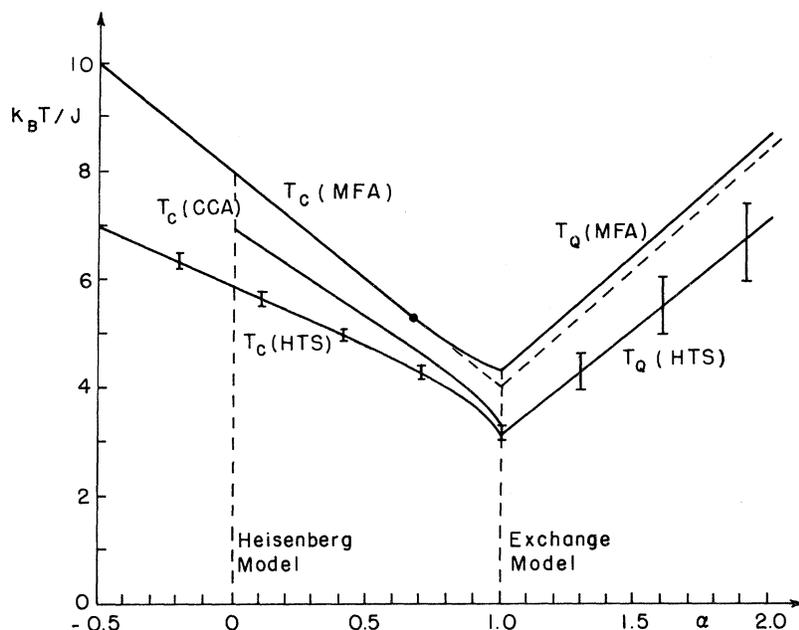
FIG. 3. Comparison of the transition temperatures T_c and T_Q for the fcc lattice as a function of the ratio of biquadratic to bilinear interaction constants α. These temperatures are obtained from high-temperature series expansions (HTS), the molecular-field approximation (MFA), and the constant-coupling approximation (CCA). The error bars give the uncertainties in the estimates from the series expansions. The dashed line gives the critical temperatures as determined from the MFA. The tricritical point in the molecular-field approximation is at $\alpha = \frac{2}{3}$.

for $\alpha > 1$. For the face-centered-cubic lattice and for $-0.5 \leq \alpha \leq 2.0$ the stability limit of the high-temperature phase (the higher of T_c and T_Q) is shown in Fig. 3. The fact that χ_2 may diverge at a higher temperature (T_Q) than χ_1 (T_c) does not necessarily mean that the system has separate dipole and quadrupole phase transitions. In the temperature range $T < T_Q$, the high-temperature series expansion for the dipole susceptibility χ_1 is not valid because it does not include the effects of the nonzero quadrupole moments on the dipole susceptibility. It is also possible to find from high-temperature series that χ_1 diverges at a higher temperature (T_c) than χ_2 (T_Q). However, this too should not be interpreted as indicating that the quadrupoles order at a lower temperature than the dipoles. This is clearly not possible because once the dipoles order in a system, the quadrupole moments will also be nonzero.

As mentioned above a first-order transition may occur at a temperature higher than the stability limit T_c or T_Q. In the molecular-field approximation the dipoles and quadrupoles order at the same temperature for $\alpha < 1$ and the transition is first order for $\frac{2}{3} < \alpha \leq 1$.[1,2] The calculation based on the constant-coupling approximation[3] shows that the transition is second order for all $\alpha \leq 1$. However, this result must be substantiated by improved calcula-

tions based on this approximation.[3] For $\alpha > 1$ the molecular-field approximation predicts a first-order quadrupolar transition. Results based on better approximations are not available for this region. To ascertain whether a first-order transition is possible it is necessary to compare the free energies of the high- and low-temperature phases of the system. If the temperature at which the free energies are equal is higher than T_c or T_Q a first-order transition occurs. We plan to investigate this possibility.

We have also analyzed these susceptibility series for the body-centered- and simple-cubic lattices. The dependence of the stability limits, T_c and T_Q, on α for these two lattices are similar to that of the face-centered-cubic lattice. However, the uncertainties in the estimates of T_c and T_q are much larger.

To summarize, we find that the critical temperatures in the region $0 \leq \alpha \leq 1$ as determined from the high-temperature series are always lower than those obtained by the molecular-field and constant-coupling approximations. For $\alpha > 1$ the stability limits of the high-temperature phase T_Q as extrapolated from the series expansions are always lower than those found in the molecular-field approximation. However, due to the relatively few terms in the series there is considerable uncertainty in our estimates of T_Q.

[1]H. H. Chen and P. M. Levy, Phys. Rev. Lett. 27, 1383 (1971); H. H. Chen and P. M. Levy, preceding paper, Phys. Rev. B 7, 4267 (1973).

[2]M. Nauciel-Bloch, G. Sarma, and A. Castets, Phys. Rev. B 5, 4603 (1972).

[3]H. A. Brown, Phys. Rev. B 4, 115 (1971). Although this

calculation takes into account the biquadratic interaction between a pair of ions it omits the interaction of the pair with the internal quadrupole field. Therefore, the results of the calculation must be regarded with some suspicion.

[4]R. I. Joseph, Phys. Rev. **138**, A1441 (1965); Phys. Rev. **163**, 523 (1967). Also see P. J. Wojtowicz and R. I. Joseph, Phys. Rev. **135**, A1314 (1964).

[5]G. A. T. Allan and D. D. Betts, Proc. Phys. Soc. Lond. **91**, 341 (1967).

[6]C. Domb, Adv. Phys. **9**, 149 (1960); H. H. Chen, Ph.D. thesis (The Johns Hopkins University, 1970), pp. 15-18 and Appendix A (unpublished).

[7]G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).

[8]In Ref. 4 the expression for a_{41} in our notation contains the term $2880P_3(5\sigma-3.024)$. This does not agree with the term in our expression $2880P_3(5\sigma-3)$.

[9]H. H. Chen and R. I. Joseph, Phys. Rev. B **2**, 2706 (1970).

[10]H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford U. P.,New York, 1971).