cubic, and bcc lattices, respectively. For $H \ll H_c$ this expression reduces to the parabolic form used above with $\gamma = \xi / H_c^2$. The correspondence of quantities in the Ising and Heisenberg Hamiltonians permits us to write $H_c = -zJ/g\mu_B$ where J is a nearest-neighbor exchange integral and z is the coordination number. Taking $g=4.9$ and $\gamma = 1.60 \times 10^{-9}$ Oe^{-2}, one finds $zJ/k = -7.6$°K and -4.8°K for $\xi = 0.87$ and $\xi = 0.35$, respectively. Treating the exchange interaction in the molecular field approximation, an analysis[16] of the paramagnetic susceptibility yields $zJ/k \sim -4$°K. Another estimate, $zJ/k = -4.6$°K, is obtained from the simple molecular field relation for the Néel temperature $T_N(0)$. It is interesting that these latter estimates of zJ/k agree best with the value deduced from the phase boundary curvature assuming ξ appropriate to a three-dimensional rather than a two-dimensional Ising model. It is not clear, however, from the limited number of cases calculated whether ξ is uniquely determined by dimensionality.

The apparent parabolic character of the phase boundary also suggests, of course, that its slope is infinite at $H=0$. It is instructive, however, to consider this slope in a somewhat different way. The thermodynamic theories of λ transitions due to Buckingham and Fairbank[11] and to Pippard,[17] adapted to magnetic state variables, yield[8]

$$C_H/T = (dH/dT)_b^2 \chi_T + K,$$

where $(dH/dT)_b$ is the slope of phase boundary. Terms referred to as K are expected not to change rapidly with T near the transition point for certain classes of systems. One may speculate that this is true of antiferromagnets such as $CoCl_2 \cdot 6H_2O$. A plot of $C_p(H=0)/T$ versus $\chi_{\|}$ extrapolated to values corresponding to $T_N(0)$ should then have a slope equal to the square of the initial slope of the antiferro-paramagnetic phase boundary for H parallel to the preferred spin direction. Such a plot was first made by Sawatzky and Bloom using earlier data for $CoCl_2 \cdot 6H_2O$ and gave paradoxical results for $T > T_N$. The analogous plot of the present data outside the region in which the λ anomaly is rounded off is shown in Fig. 5. It yields curves which approach vertical asymptotes both above and below $T_N(0)$. An ideal crystal of $CoCl_2 \cdot 6H_2O$ might thus be expected to exhibit a sharp phase boundary with essentially infinite initial slope at $H=0$, as anticipated above. This analysis removes the paradox noted by Sawatzky and Bloom. It suggests also that the state of the real crystal in the interval $\Delta T \sim 10^{-2}$ °K about T_N may have no simple thermodyanmic description possibly because of spatial inhomogenity of the system. Thus it might prove difficult to reconcile microscopic effects seen by resonance techniques within this interval with macroscopic thermodynamic quantities.

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New Expansion for the Classical Heisenberg Model and its Similarity to the $S=\frac{1}{2}$ Ising Model

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The zero-field susceptibility of the classical Heisenberg model is expanded in the new expansion parameter $u \equiv \mathcal{L}(2J/kT)$ and a formal similarity with the $S=\frac{1}{2}$ Ising-model expansion is noted. The new Heisenberg-model expansion is seen to provide more reliable extrapolations (especially for one- and two-dimensional lattices) than heretofore, and to permit comparison with Brown's recent work on the Bethe-Peierls approximation.

The zero-field reduced susceptibility $\bar{\chi}^I \equiv \chi^I / \chi_{\text{Curie}}^I$ of the $S=\frac{1}{2}$ Ising model has been developed by Oguchi[1] as a power series in the variable $v \equiv \tanh K$, where $K \equiv 2J/kT$ and $-2J$ is the interaction energy of nearest-neighbor spins. This suggests that there might exist better expansion parameters than the parameter K (customarily used) for the reduced susceptibility

$$\bar{\chi}^H = 1 + \sum_{n=1}^{\infty} a_n (\tfrac{1}{2}K)^n \tag{1}$$

of the classical ($S=\infty$) Heisenberg model.[2,3]

Here we propose the new expansion parameter $u \equiv \mathcal{L}(K) = \coth K - 1/K$, motivated (in part) by the similarity between the exact expressions

$$\bar{\chi}^I = (1+v)/(1-v), \tag{2a}$$

and

$$\bar{\chi}^H = (1+u)/(1-u) \tag{2b}$$

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[2] H. E. Stanley and T. A. Kaplan, Phys. Rev. Letters **16**, 981 (1966); P. J. Wood and G. S. Rushbrooke, *ibid.* **17**, 307 (1966); G. S. Joyce and R. G. Bowers, Proc. Phys. Soc. (London) **88**, 1053 (1966).
[3] H. E. Stanley, Phys. Rev. **158**, 546 (1967). There is a misprint in Eq. (3): The first summation should be restricted to pairs of nearest-neighbor spins.

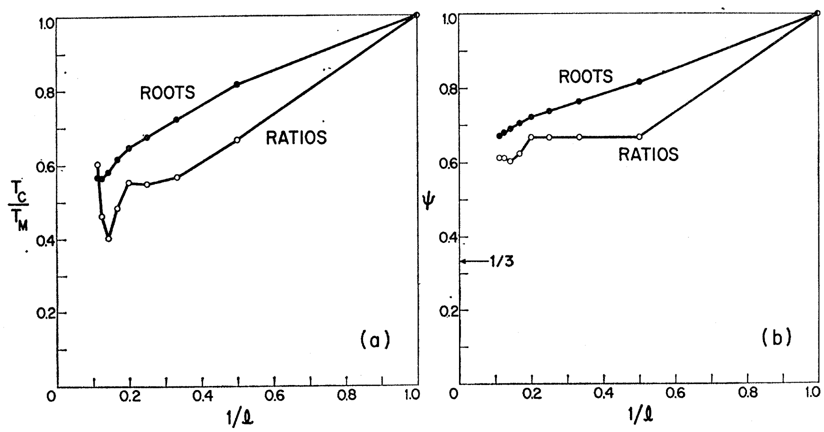

FIG. 1. Honeycomb lattice ($z=3$) for classical ($S=\infty$) Heisenberg model: (a) The ratios a_l/a_1a_{l-1} and lth roots $(\sqrt[l]{a_l})/a_1$ for the coefficients in Eq. (1). (b) The ratios A_l/A_1A_{l-1} and lth roots $(\sqrt[l]{A_l})/A_1$ for the coefficients in Eq. (3). Since $A_1=z$,

$$\psi\equiv\lim_{l\to\infty}A_l/A_1A_{l-1}\equiv\lim_{l\to\infty}(\sqrt[l]{A_l})/A_1$$
$$=(zu_c)^{-1}=\{z\mathcal{L}[(3/z)(T_M/T_c)]\}^{-1}.$$

For example, if for the honeycomb net $\psi=\frac{1}{3}$, then $T_c/T_M=0$; if $\psi=0.6$, then $T_c/T_M\cong 0.5$.

for the $S=\frac{1}{2}$ Ising and $S=\infty$ Heisenberg linear chains. We have calculated the coefficients A_n in the new expansion

$$\tilde{\chi}^H=1+\sum_{n=1}^{\infty}A_n u^n \qquad (3)$$

through order $n=8$ for general crystal structures (and through order $n=9$ for the subclass of loose-packed lattices). The coefficients A_n are obtained from the general-lattice expressions[3] for the a_n using the small-argument expansion $\mathcal{L}(K)=\frac{1}{3}K-\frac{1}{45}K^3+\cdots$ of the right-hand side of Eq. (3).[4]

Besides having developed the new expansion (3), we have made the observations listed in Secs. I and II below.

I. UTILITY FOR ESTIMATING CRITICAL PROPERTIES

The radii of convergence $u_c=\mathcal{L}(K_c)$ of Eq. (3) (as estimated by standard extrapolation procedures) agree with the radii of convergence K_c, estimated from the conventional expansion (1), for all two- and three-dimensional lattices studied. Moreover, the behavior of the new coefficients A_n is generally smoother than that of the coefficients a_n in the old expansion (1), thereby increasing the (subjective) reliability of extrapolations based thereon.

[*Note added in proof.* For the fcc and bcc three-dimensional lattices, the evidence that $\gamma=1.38$ ($\cong 11/8$, as some may prefer) is strengthened. Whereas for the sc lattice the new series, like the old, is less smooth than for the fcc and bcc, it is nevertheless quite plaus-

TABLE I. General-lattice expressions for the D_n^H through order $n=8$ (through order $n=9$ for the subclass of loose-packed lattices).

$D_3^H=-6p_3$

$D_4^H=-8p_4-4.8p_3$

$D_5^H=-10p_5-6.4p_4+7.92p_3+4.8p_{5a}$

$D_6^H=-12p_6-8p_5+10.56p_4+(133.2/7)p_3+4.8(p_{6a}+p_{6b})+8p_{6c}+42.72p_{5a}$

$D_7^H=-14p_7-9.6p_6+13.2p_5+(33.792/7)p_4+(83.52/7)p_3+4.8(p_{7a}+p_{7b}+p_{7f})+10.56p_{7c}+8(p_{7d}+p_{7e})+79.2p_{7g}$
$+17.28p_{6a}+46.32p_{6b}+28.8p_{6c}+20.736p_{6d}+(823.392/7)p_{5a}$

$D_8^H=-16p_8-11.2p_7+15.84p_6+(42.24/7)p_5+(141.504/7)p_4-(1071.792/49)p_3+4.8(p_{8a}+p_{8b}+p_{8c}+p_{8d})+10.56(p_{8e}+p_{8f}+p_{8p})$
$+8(p_{8g}+p_{8h}+p_{8j}+p_{8k})+14.4p_{8l}+6.912p_{8q}+86.4(p_{8r}+p_{8s})+49.92(p_{7a}+p_{7b})+106.752p_{7c}+28.8(p_{7d}+p_{7e})$
$+17.28p_{7f}+(815.04/7)p_{7g}+17.28p_{7h}+139.968p_{6a}+(627.84/7)p_{6b}+33.6p_{6c}+74.88p_{6d}+(140.640/7)p_{5a}$

$D_9^H=-12.8p_8+(50.688/7)p_6+(138.0684/7)p_4+4.8(p_{9k}+p_{9l})+8p_{9j}+10.56p_{9m}+17.28p_{8c}+28.8p_{8h}+149.76p_{8r}+13.824p_{8t}$
$+(368.448/7)p_{7a}+(813.312/7)p_{6a}$

[4] The first three A_n are identical for both the classical Heisenberg model and the $S=\frac{1}{2}$ Ising-model expansions: $A_1=3a_1/2=z$, $A_2=9a_2/4=z\sigma$, and $A_3=27a_3/8+3A_1/5=z\sigma^2-6p_3$ (notation as in Ref. 3). The general lattice expressions for the higher-order A_n become increasingly complex; they are not given here, but *may* be obtained directly from Table I (see Ref. 10).

ible[5] that γ should also be 1.38 (in contrast to the rather more crude estimate of 1.4 proposed[3] on the basis of the old expansion).]

For the two-dimensional plane triangular, square and honeycomb lattices, the new coefficients behave more regularly and indicate a phase transition at a value of the critical temperature which is appreciably different from zero. Even for the *least* regular of these three lattices, the honeycomb, the sequences of ratios A_n/A_{n-1} and roots $(A_n)^{1/n}$ [Fig. 1(b)] are somewhat smoother than the corresponding sequences a_n/a_{n-1} and $(a_n)^{1/n}$ [Fig. 1(a)].

For the one-dimensional lattice (linear chain), the coefficients a_n behave so irregularly with n that it would seem the radius of convergence cannot be estimated by extrapolation. However, the new coefficients A_n *do* behave smoothly [$A_n=2$ for $n\geq 1$] for the linear chain, and indeed predict the exact value for the radius of convergence, $u_c=1$ ($K_c=\infty$, or $T_c=0$). This is relevant, as the case for the existence of a phase transition ($T_c>0$) for the two-dimensional classical Heisenberg model[3,6] is somewhat strengthened now that high-temperature expansions "give correct answers" in one dimension as well as in three dimensions.

II. RELATION TO THE BETHE-PEIERLS APPROXIMATION

It is well known that in the Bethe-Peierls approximation[7]

$$\bar{\chi}^I=(1+v)/(1-\sigma v), \tag{4a}$$

and[8]

$$\bar{\chi}^H=(1+u)/(1-\sigma u), \tag{4b}$$

where $\sigma\equiv z-1$, and z is the lattice coordination number. This suggests the following expansions of the exact Ising[9] and Heisenberg models:

$$\bar{\chi}^I=(1-\sigma v)^{-2}[1-(\sigma-1)v-\sigma v^2+\sum_{n=3}^{\infty}D_n{}^Iv^n] \tag{5a}$$

and

$$\bar{\chi}^H=(1-\sigma u)^{-2}[1-(\sigma-1)u-\sigma u^2+\sum_{n=3}^{\infty}D_n{}^Hu^n]. \tag{5b}$$

Whereas the A_n were rather unwieldy functions of the basic lattice constants p_{mx} [involving each p_{mx} multiplied by a complicated $(n-m)$th-order polynomial in σ],[4] the coefficients D_n are quite simple *and are independent of* σ. The $S=\frac{1}{2}$ Ising-model coefficients $D_n{}^I$ are given in Ref. 9; Table I lists the $D_n{}^H$ for the classical Heisenberg model.[10]

Brown[11] has very recently studied the critical properties of the Heisenberg ferromagnet with the aid of the Bethe-Peierls approximation; some of his results disagree with extrapolations based upon high-temperature expansions. For example, Brown points out[11] that Eq. (4b) predicts $\gamma=1$ in the assumed form of the divergence of χ, $\chi\sim(T-T_c)^{-\gamma}$ as $T\rightarrow T_c{}^+$, whereas high-temperature techniques suggest $\gamma\cong1.4$ for some lattices. The source of this disagreement can be seen from Eq. (5b) and Table I: All of the coefficients D_n become zero for a lattice which has no polygons or other "closed circuits,"[12] and Eq. (5b) reduces to Eq. (4b). Thus, it would appear that the Bethe-Peierls result (4b) is *exact* for lattices with no closed circuits. The common (multiply connected) crystal structures found in nature possess many closed circuits, and the D_n are by no means zero. Thus, including terms in the high-temperature expansion (5b) *beyond* order $n=2$ corresponds, in some sense, to taking account of the "multiple connectivity" of the lattice, and one might expect extrapolations based upon high-temperature expansions carried beyond second order to be more realistic than the Bethe-Peierls approximation.

III. CONCLUSION

We conclude by noting that many of the above remarks also apply to the Vaks-Larkin model and to the high-temperature expansions of the internal energies $E^I\sim\sum_n B_n{}^Iv^n$ and $E^H\sim\sum_n B_n{}^Hu^n$ of the $S=\frac{1}{2}$ Ising, and $S=\infty$ Heisenberg models. These observations will be developed at greater length elsewhere.

[5] Also the value $\gamma=1.43(\cong10/7)$ proposed [G. A. Baker, H. E. Gilbert, J. Eve, and G. S. Rushbrooke, Phys. Letters **20**, 146 (1966)] for the $S=1/2$ Heisenberg model is not supported in this $S=\infty$ (classical) limit; hence it would appear that γ is indeed *spin-dependent*. However, the "mnemonic formula" $\gamma(S)=1.33+0.05/S$ [H. E. Stanley and T. A. Kaplan, J. Appl. Phys. **38**, 977 (1967)] must certainly be revised in the light of the additional terms now available and the more sophisticated extrapolation procedures explained in Ref. 3. Whether γ should vary smoothly and continuously from its value at $S=1/2$ to its value at $S=\infty$ is not clear at present; however, a preliminary calculation indicates that $\gamma(S)\cong1.38$, for all $S>1/2$. It is important to realize that the above work is restricted to fcc, bcc, and sc lattices; indeed, extrapolations based upon the new expansion (3) strengthen the evidence that γ is appreciably *less* than 4/3 for the spinel lattice with nearest-neighbor ferromagnetic interactions between B-site cations.

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[7] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935); R. Peierls, *ibid.* **A154**, 207 (1936).

[8] H. A. Brown, J. Phys. Chem. Solids **26**, 1369 (1965). M. E. Fisher, Am. J. Phys. **32**, 343 (1964); N. W. Dalton, Proc. Phys. Soc. (London) **89**, 845 (1966).

[9] M. F. Sykes [J. Math. Phys. **2**, 52 (1961)] has carried out the expansion (5a) for the Ising model.

[10] The coefficients A_n may be recovered from the D_n of Table I by means of the recursion relation $A_n=D_n+2\sigma A_{n-1}-\sigma^2A_{n-2}$; the a_n of Eq. (1) may be recovered in turn from the A_n using the small-argument expansion of $\mathfrak{L}(K)$. Thus, these general lattice expressions for the D_n contain all of the information contained in the (much more lengthy) general lattice expressions for the a_n presented in Table I of Ref. 3. *Note*: we have extended the calculation of Ref. 3 to include close-packed lattices in eighth order. Of particular current interest (cf. Ref. 6) are the coefficients for the (close-packed) plane triangular lattice; the previously unreported coefficient in the conventional series (1) is $a_8=4351.6775$.

[11] H. A. Brown, Bull. Am. Phys. Soc. **12**, 502 (1967).

[12] The linear chain provides an example of a lattice with no closed circuits, and Eqs. (4a) and (4b) indeed reduce to Eqs. (2a) and (2b) upon setting $\sigma\equiv z-1=1$.