Axial next-nearest-neighbor Ising (ANNNI) and extended-ANNNI models in external fields

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I consider the phase structure of the axial next-nearest-neighbor Ising (ANNNI) model and the axial third-nearest-neighbor Ising (A3NNI) model in the presence of a uniform external field. A mean-field calculation is used, and special attention is paid to possible implications for a phenomenological application of the A3NNI model to ferroelectric materials with modulated phases.

I. INTRODUCTION

The axial next-nearest-neighbor Ising (ANNNI) model has recently received extensive attention due to the intricacy of its phase structure and to the great amount of interesting physical effects present.[1-6] Although there are numerous compounds exhibiting the modulated phases arising in the ANNNI models, most work has concentrated on the theoretical aspects and made no attempt at any phenomenological application. This is due, at least in part, to the facts that the theoretical situation is still somewhat unsettled and that the model seemingly is too simple to handle the complexities of the real world. One exception is the work by Yamada and Hamaya,[2] who were able to explain the phase structure of a large number of ferroelectric materials by using an ANNNI model extended to include third-nearest-neighbor interactions, an axial third-nearest-neighbor Ising (A3NNI) model. For one class of compounds they also found it necessary to include an additional, uniform-strain term in the Hamiltonian in order to reproduce the observed phases. This suggests an investigation of the model in a uniform external field. For this reason, as well as for the inherent theoretical interest, we have calculated the phase structure for both the ANNNI and A3NNI models in the presence of an external field.

The calculation is based on the mean-field method developed for the ANNNI model by Bak and von Boehm.[3] The inclusion of an applied field has already been done by Yokoi, Coutinho-Filho, and Salinas,[4] who used it to calculate H-T phase diagrams for the ANNNI model (H representing the imposed field). What we shall calculate are T-J_2 phase diagrams for both ANNNI and A3NNI models for fixed values of the field.

The model is defined as follows. Sites of a cubic lattice are occupied by spins which can assume the values ± 1. There is some preferred z axis, and it is assumed that all spins in each layer perpendicular to the z axis are the same. This effectively reduces the problem to a one-dimensional model including self-interactions, with Hamiltonian

$$\mathcal{H}=-\sum_{\text{pairs }(i,j)} J_{ij}s_i s_j - h_0\sum_i s_i - J_0\sum_i s_i^2 , \tag{1}$$

where the subscript i or j labels the position along the z axis and where J_0 is the net interaction with all other spins in the same layer. The cases considered here are the standard ANNNI model, with $J_0,J_1,J_2\neq 0$, and the A3NNI model, with $J_0,J_1,J_2,J_3\neq 0$. In the ANNNI model we follow Bak and von Boehm[3] and consider $J_1>0$ (ferro), $J_2<0$ (antiferro), whereas in the A3NNI case we choose $J_1,J_2<0$, $J_3>0$ in order to maintain contact with Ref. 2. In both cases we take $|J_1|=1.0$ to set the one scale in the problem and choose $J_0=4.0$.

II. ANNNI MODEL

We consider first the ANNNI model, to establish and review the techniques used as well as to present the result for the phase diagram. The treatment follows that of Ref. 4 although there are minor differences in notation. The standard mean-field equation with which we shall be working is

$$\begin{aligned}&\langle s_i\rangle=\tanh[\beta(H_i+h_0)] ,\\ &H_i=\sum_j J_{ij}\langle s_j\rangle ,\end{aligned} \tag{2}$$

where h_0 is the applied field. In the absence of an external field ($h_0=0$), $\langle s_i\rangle=0$ is always a solution of (2), and for high temperature it is the only solution. As the temperature is reduced, one reaches the critical temperature (T_c), at which a nonzero solution is also possible. One determines T_c by expanding the tanh in Eq. (1) for small argument, Fourier transforming, and finding the maximum $T(\equiv T_c)$ for which a solution exists. This leads to the familiar equations:

$$\begin{aligned}&J(q)=J_0+2J_1\cos(qa)+2J_2\cos(2qa) ,\\ &T_c=\max_q J(q)\equiv J(q_c) ,\\ &q_c=\begin{cases}0, & -J_1/4J_2\geq 1\\ \dfrac{1}{a}\cos^{-1}\left[\dfrac{-J_1}{4J_2}\right], & -J_1/4J_2\leq 1\end{cases}\end{aligned} \tag{3}$$

for the critical temperature of the disordered to the modulated phase transition in the absence of an external field.

When $h_0\neq 0$, Eq. (2) does not admit the zero solution,

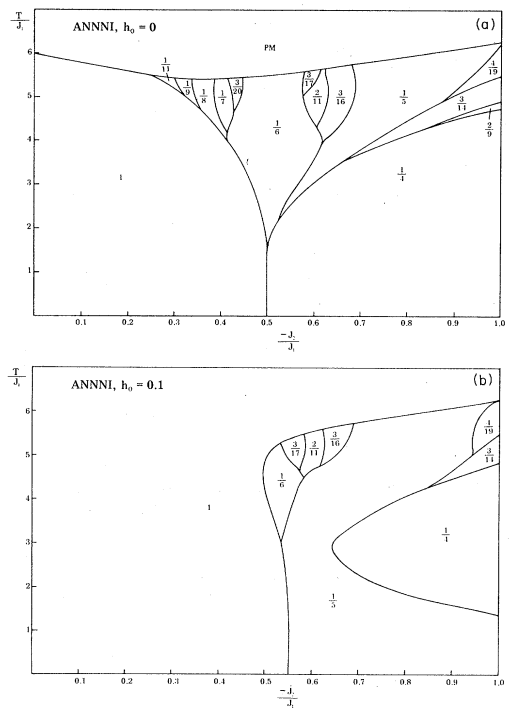

FIG. 1. Mean-field phase diagrams for the ANNNI model: (a) without applied field; (b) with applied field $h_0=0.1$.

but there is still a spatially uniform solution, $\langle s_i\rangle=s_0$,

$$s_0(T)=\tanh\{\beta[J(q=0)s_0(T)+h_0]\}\ . \tag{4}$$

For high temperature we can expand around s_0, $\langle s_i\rangle=s_0+\delta s_i$, and again expand the tanh in Eq. (2). That leads to

$$T_c=[1-s_0^2(T_c)]J(q_c)\ , \tag{5}$$

where $J(q)$ and q_c are as in (2), and where $s_0(T_c)$ is obtained by solving Eq. (4) self-consistently with Eq. (5).

The foregoing determines the line separating the paramagnetic phase from the modulated phases. To calculate the correct modulated phase for a given T and J_2 we follow the procedure of Bak and von Boehm.[3] One assumes that the spin structure repeats itself after N layers and solves Eq. (2) iteratively. The solution obtained is used to calculate the free energy per spin for that N:

$$F(N,T)=\frac{1}{N}\sum_{j=0}^{N-1}(-T\ln\{2\cosh[\beta(H_j+h_0)]\}+\tfrac{1}{2}\langle s_j\rangle H_j)\ . \tag{6}$$

This is done for a range of N (1—20), and the N with the minimum free energy per spin is the stable phase at that temperature and J_2. We have carried out this procedure and show the resulting phase diagrams in Fig. 1. Figure 1(a) is just the Bak—von Boehm result[3] for no applied field, while Fig. 1(b) shows the effect of the external field. The number labeling each phase is its periodicity, and as usual only the more important phases are shown. Note that once a nonzero field is applied, the disordered phase disappears entirely since $\langle s_i\rangle=0$ no longer solves Eq. (2). As one would expect, the external field tends to stabilize those phases with the largest magnetizations $(1,\frac{1}{5})$.

III. A3NNI MODEL

The calculation here proceeds as in the ANNNI case, except that the J_{ij}'s and therefore $J(q)$, are different. The result for the critical temperature of the disordered to modulated phase transition is now

$$J(q)=J_0+2J_1\cos(qa)+2J_2\cos(2qa)+2J_3\cos(3qa)\ , \tag{7}$$

$$T_c=J(q_c)\ ,$$

for $h_0=0$, and

$$T_c=[1-s_0^2(T_c)]J(q_c)\ ,\qquad s_0(T)=\tanh\{\beta[J(q=0)s_0+h_0]\}\ , \tag{8}$$

in the presence of an external field, with

$$q_c=\begin{cases}\pi\ , & 4J_2>(9J_3+J_1)\\ \dfrac{1}{a}\cos^{-1}\left[-\tfrac{1}{2}\left\{\dfrac{J_2}{3J_3}+\left[\left\{\dfrac{J_2}{3J_3}\right\}^2+1-\dfrac{J_1}{3J_3}\right]^{1/2}\right\}\right]\ , & 4J_2\le(9J_3+J_1)\end{cases} \tag{9}$$

in either case.

The calculation of which is the stable modulated phase at a particular T and J_2 also follows the ANNNI calculation, except that for the moment we limit ourselves to $N\le 17$ in order to facilitate comparison of our results to previous work.[2] (We shall return to this point below.) Also for purposes of comparison, we take $J_3=+0.1$. The resulting phase diagrams are shown in Fig. 2. Figure 2(a) is the $h_0=0$ result, which agrees with Ref. 2, and Figs. 2(b) and 2(c) are for $h_0=0.1$ and 0.5, respectively.

As mentioned above, the A3NNI model has been used to explain the phase structure of a large number of ferroelectric materials exhibiting modulated phases.[2] If one accepts the results of Ref. 2, then our work provides an interesting additional test of the phenomenological applicability of the A3NNI model, since we have calculated how the phase diagram changes when an external field is applied. In fact, a brief inspection reveals that the effect of an applied field could be quite dramatic. With no applied field Rb_2ZnBr_4 goes from a $\frac{6}{17}$ phase, through an in-

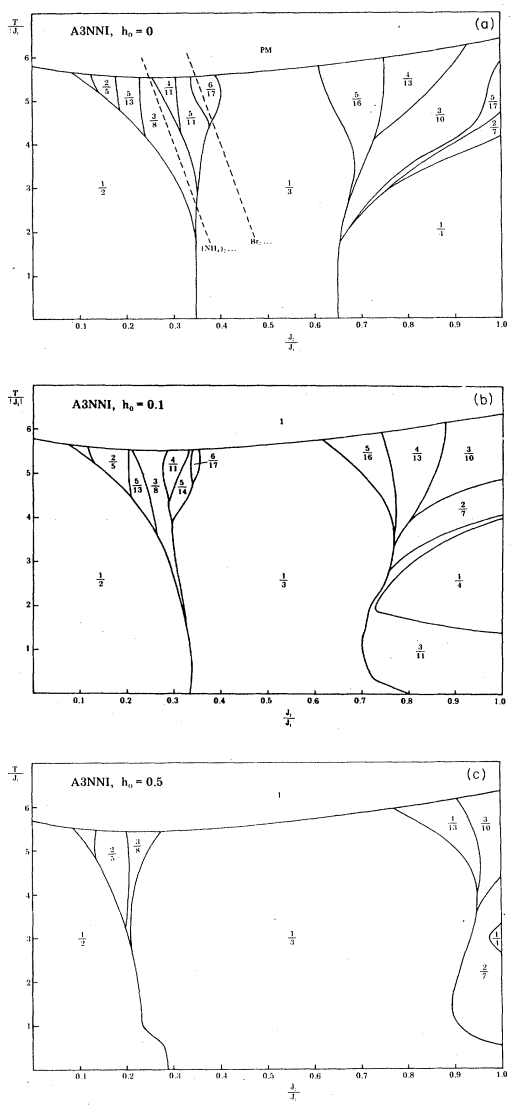

FIG. 2. Mean-field phase diagrams for the A3NNI model with (a) $h_0=0$; (b) $h_0=0.1$; (c) $h_0=0.5$. A maximum repetition length $N_{\max}=17$ was used.

commensurate phase, to a $\frac{1}{3}$ phase;[7,8] and $(NH_4)_2ZnCl_4$ goes from $\frac{3}{8}$ to $\frac{1}{3}$ (Ref. 9) as the temperature is reduced.[10] The behavior of the two materials corresponds nicely to the dashed lines on Fig. 2(a), where the lines are drawn at an angle in order to include an assumed temperature dependence of J_2/J_1.[2] Referring to Fig. 2(b) we see that in the external field the $\frac{6}{17}$ phase of Rb_2ZnBr_4 shrinks away (almost) entirely. On the other hand, the sequence of phases of $(NH_4)_2ZnCl_4$ could very well remain the same, except for the actual transition temperatures. From the diagram it is even possible that $(NH_4)_2ZnCl_4$ would develop a range of the $\frac{5}{14}$ phase in an applied field. As for the applied field needed to observe this effect, a crude estimate can be made using known transition temperatures of Rb_2ZnBr_4 (Ref. 7) to fix the scale of T and therefore J_1, and using measured lattice spacings.[8] It suggests that $h_0=0.1J_1$ corresponds to an electric field of around 10^6 V/m.

Flaws appear, however, when we examine details of the phenomenological facade. One of them is the ordering of the temperatures at which the transitions occur. The $\frac{3}{8}$ to $\frac{1}{3}$ transition for $(NH_4)_2ZnCl_4$ occurs around 270 K; and the $\frac{6}{17}$ to incommensurate to $\frac{1}{3}$ transitions in Rb_2ZnBr_4 occur at 199 K and 190 K, respectively. On the phase diagram, however, the $\frac{3}{8}$ phase abuts the $\frac{1}{3}$ phase at a *lower* temperature than does $\frac{6}{17}$. Thus the present choice of parameters cannot describe both materials in quantitative detail. The simplest modification would be to ascribe a different value of J_1 to one of the materials while keeping all J_i/J_1 unchanged, thereby changing the relative temperature scales.

A more serious embarrassment arises when, in the calculation of the phase diagram, one allows repetition lengths up to 20 instead of only 17. Then the phase diagram appears as in Fig. 3. The crucial change from Fig. 2(a) is that the $\frac{6}{17}$ phase no longer adjoins the $\frac{1}{3}$ phase, and consequently the behavior of Rb_2ZnBr_4 is not correctly reproduced. It is quite possible that this could be remedied by a change in the value of J_3, but until that is shown the detailed quantitative application of the model has a difficulty.

There is an interesting new qualitative consequence of this work.[11] Certain materials, notably $BaMnF_4$ and $Ba_2NaNb_5O_{15}$,[12] are ferroelectric not just in the modulated phases but throughout the measured temperature range. This indicates the presence of an internal field which is not linked to the modulated structure and which could therefore be modeled by an external field in the context of the A3NNI model. The interesting point is that the external field stabilizes phases which are not ($T=0$) ground states in the A3NNI model in zero field. That opens the possibility of describing materials whose low-temperature phase is other than the simple 1, $\frac{1}{2}$, $\frac{1}{3}$, or $\frac{1}{4}$ of the ANNNI or A3NNI models with no applied field. In particular, we may be able to understand $BaMnF_4$, which locks into the $\frac{3}{10}$ phase at low T. For the parameters of Fig. 2(b) we see that the $\frac{3}{11}$ phase is stable. It is also possible to find values of the parameters such that the $\frac{3}{10}$ phase is the ground state for a significant range of

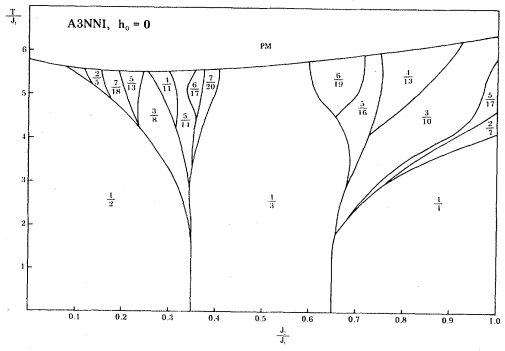

FIG. 3. A3NNI phase diagram in absence of external field, allowing repetition lengths up to $N_{\max}=20$.

J_2/J_1. As an example, for $h_0=0.01J_1$, $J_3=0.1$, the ground state is $\frac{3}{10}$ over a range of about 0.1 in J_2/J_1 centered around $J_2/J_1\approx 0.9$. We do not yet have a phase diagram similar to those of Figs. 1 and 2 on which the full phase structure of $BaMnF_4$ is correctly reproduced, but it is possible that we shall in the future.

IV. CONCLUSIONS

We have calculated phase diagrams for both the ANNNI and A3NNI models in the presence of a uniform external field. We have also discussed possible phenomenological relevance, including some difficulties with detailed quantitative applications and possible ways of overcoming or circumventing these difficulties. The most interesting practical aspect at present appears to be the potential for understanding the phase structure of $BaMnF_4$.

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