New types of reentrant phase transitions in the singlet-triplet model of antiferromagnets

P. Pawlicki
Institute of Physics, A. Mickiewicz University, Matejki 48/49, PL-60-769 Poznań, Poland

R. Micnas*
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, Boite Postale 166X, 38042 Grenoble Cédex, France

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New theoretical possibilities of temperature-induced antiferromagnetic ordering in the singlet-triplet model are considered. Within the framework of mean-field theory the phase diagrams in the temperature–magnetic-field plane have been determined. They exhibit several possibilities of reentrant phase transitions to the paramagnetic and to the antiferromagnetic phases, as well as several multicritical points. One of the phase diagrams is a simplified version of the case of HoSb.

I. INTRODUCTION

In the present work we study the new theoretical possibilities of so-called heat magnetization in a system of magnetic moments influenced by a cubic crystal field. This phenomenon was predicted for the first time by Kitano and Trammell[1] for the case where the lowest-lying crystal-field-only state is a singlet while the next one is a triplet. The physical reason for the occurrence of ferromagnetic long-range order with increasing temperature in such a system is the following.[2] At zero temperature the unmagnetized singlet lies lower than the triplet if the exchange interaction is not large enough to overcome the crystal-field splitting. With increasing temperature the excited triplet state becomes increasingly populated. If at some finite temperature magnetic long-range order occurs then the exchange field becomes larger and the triplet is split. This in turn gives rise to magnetization in a self-consistent manner. The appearance of the heat magnetization can sometimes assume the nature of a first-order phase transition,[3] which was overlooked in the original work of Kitano and Trammell.[1]

In the subsequent sections we investigate the antiferromagnetic version of heat magnetization in the singlet-triplet model, by using the mean-field theory. It will be shown further that this case includes new, interesting properties which have no simple relevance to the ferromagnetic case considered earlier.[1–3]

II. THE MODEL

We consider the two-sublattice Ising antiferromagnet with magnetic moments influenced by a cubic crystal field. The model Hamiltonian is the following:

$$\hat{H}=\sum_{\alpha}V_{\alpha}^{c}+\sum_{\beta}V_{\beta}^{c}-H\sum_{\alpha}J_{\alpha}^{z}-H\sum_{\beta}J_{\beta}^{z}$$
$$-K\sum_{\alpha,\beta}J_{\alpha}^{z}J_{\beta}^{z}-L\sum_{\alpha,\alpha'}J_{\alpha}^{z}J_{\alpha'}^{z}-L\sum_{\beta,\beta'}J_{\beta}^{z}J_{\beta'}^{z}\ . \quad (1)$$

Here $V_{\alpha,\beta}^{c}$ are the crystal-field operators acting upon the variables of the first and second sublattices, yielding the singlet ground state and the triplet excited states separated by an energy gap Δ, J^{z} are the z components of the total angular momentum of each ion, α and β are the indices labeling the first and second sublattices, respectively, K is the inter- and L the intra-sublattice exchange interaction, and H is the external magnetic field measured in energy units. We assume that $K<0$ (antiferromagnetic coupling) and $L>0$ (otherwise the sublattice structure would be unstable).

The free energy of the system is calculated by using the Bogoliubov variational principle.[4] To begin with we specify the trial Hamiltonian as follows:

$$\hat{H}_{0}=\hat{H}_{1}^{0}+\hat{H}_{2}^{0}=\sum_{\alpha}(V_{\alpha}^{c}-H_{\alpha}J_{\alpha}^{z})+\sum_{\beta}(V_{\beta}^{c}-H_{\beta}J_{\beta}^{z})\ , \quad (2)$$

$H_{\alpha,\beta}$ being the effective fields along the z axis. The free energy is then given by

$$F=-k_{B}T\ln\mathrm{Tr}\exp\left[-\frac{\hat{H}_{0}}{k_{B}T}\right]+\langle\hat{H}-\hat{H}_{0}\rangle_{0}\ , \quad (3)$$

where $\langle\ \rangle_{0}$ denotes the expectation value with respect to the Hamiltonian $\hat{H}_{0}$ acting in the product space of the four-dimensional spaces spanned by the eigenkets of the corresponding crystal-field operators $V_{\alpha,\beta}^{c}$. The representation of these states in the manifold of constant angular momentum J can be found, for example, in Leushin's tables.[5] The nonzero matrix elements $\bar{\alpha}$ and $\bar{\beta}$ of the J^{z} operator for all possible singlet-triplet spaces up to $J=8$ are listed in Table I. After evaluating the free energy, Eq. (3), we minimize this function with respect to the molecular fields H_{α} and H_{β} which gives

$$H_{\alpha}=H+z_{1}Km_{2}+z_{2}Lm_{1}\ , \quad (4a)$$

$$H_{\beta}=H+z_{1}Km_{1}+z_{2}Lm_{2}\ , \quad (4b)$$

where z_{1},z_{2} are the coordination numbers of the first and second neighbors, and m_{1},m_{2} denote the sublattice magnetizations. The final form of the free energy per site is given by

$$f=-t\ln\left\{2e^{-1/t}\cosh\left[\frac{h_1}{t}\right]+2e^{-1/2t}\cosh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_1^2\right]^{1/2}\right]\right\}$$
$$-t\ln\left\{2e^{-1/t}\cosh\left[\frac{h_2}{t}\right]+2e^{-1/2t}\cosh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_2^2\right]^{1/2}\right]\right\}+2cy^2+\frac{a}{2c}x^2\ , \tag{5}$$

where

$$h_{1,2}=h+2cy\pm x\ , \tag{6}$$

$$x=\frac{\bar{\beta}(L-K)}{2\Delta}(m_1-m_2),\quad y=\frac{m_1+m_2}{2\bar{\beta}},\quad t=\frac{k_BT}{\Delta},\quad h=\frac{\bar{\beta}H}{\Delta}\ , \tag{7}$$

$$a=\frac{L+K}{L-K},\quad b=\frac{2\bar{\alpha}^2(L+K)}{\Delta},\quad c=\frac{\bar{\beta}^2(L+K)}{2\Delta}\ . \tag{8}$$

Here x and y are the antiferromagnetic and ferromagnetic order parameters, respectively. In equilibrium they should minimize the free energy; i.e.,

$$\frac{\partial f}{\partial x}=\frac{\partial f}{\partial y}=0\ . \tag{9}$$

It can easily be shown that these equations are equivalent to

$$\frac{\partial f}{\partial m_1}=\frac{\partial f}{\partial m_2}=0\ . \tag{10}$$

The order parameters x and y obtained from (9) satisfy the following self-consistent equations:

$$\frac{a}{c}x+2y=2\frac{e^{-1/4t}\sinh\left[\frac{h_1}{t}\right]+e^{1/4t}\left\{\sinh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_1^2\right]^{1/2}\right]\right\}\frac{bh_1}{2c(1+bh_1^2c^{-1})^{1/2}}}{e^{-1/4t}\cosh\left[\frac{h_1}{t}\right]+e^{1/4t}\cosh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_1^2\right]^{1/2}\right]}\ , \tag{11a}$$

$$\frac{a}{c}x-2y=-2\frac{e^{-1/4t}\sinh\left[\frac{h_2}{t}\right]+e^{1/4t}\left\{\sinh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_2^2\right]^{1/2}\right]\right\}\frac{bh_2}{2c(1+bh_2^2c^{-1})^{1/2}}}{e^{-1/4t}\cosh\left[\frac{h_2}{t}\right]+e^{1/4t}\cosh\left[\frac{1}{2t}\left[1+\frac{b}{c}h_2^2\right]^{1/2}\right]}\ . \tag{11b}$$

We notice that the number of the model parameters is now reduced from five (K, L, Δ, $\bar{\alpha}$, $\bar{\beta}$) to three (a, b, c). At zero temperature the free energy is given by

$$f=\omega_\alpha+\omega_\beta+2cy^2+\frac{a}{2c}x^2\ , \tag{12}$$

where ω_α and ω_β are the eigenenergies of the Hamiltonians $\hat{H}_1^0$ and $\hat{H}_2^0$, respectively. There are four possibilities for ω_α:

$$\omega_\alpha^0=\frac{1}{2}-\frac{1}{2}\left[1+\frac{b}{c}h_1^2\right]^{1/2}\ ,$$
$$\omega_\alpha^1=1-h_1\ ,$$
$$\omega_\alpha^2=\frac{1}{2}+\frac{1}{2}\left[1+\frac{b}{c}h_1^2\right]^{1/2}\ , \tag{13}$$
$$\omega_\alpha^3=1+h_1\ ,$$

while the expressions for ω_β are obtained from Eq. (13) upon replacing $h_1\rightarrow h_2$. The quantities $\omega_{\alpha,\beta}$ have the meaning of the molecular-field energy levels per one site and only the lowest-lying states of the first and second sublattice contribute to the free energy (12), depending on the model parameters a, b, c and the magnetic field.

III. CONDITIONS FOR HEAT ORDERING

In order to obtain heat ordering the two following conditions should be fulfilled simultaneously. The first one is that the ground state ($T=0$, $H=0$) should be nonmagnetic and the second is that at higher temperature antiferromagnetic ordering should occur. Let us begin with the ground-state considerations.

It follows from Eq. (12) that the stability of the free energy requires that $a,c>0$ which in turn implies also $b>0$ because of Eq. (8). Existence of the antiferromagnetic

TABLE I. The nonzero matrix elements of the J^z operator in the manifold of the singlet Γ^0 and triplet $\Gamma^{1,2,3}$ states: $\bar{\alpha}=\langle\Gamma^0|J^z|\Gamma^2\rangle=\langle\Gamma^2|J^z|\Gamma^0\rangle$, $\bar{\beta}=\langle\Gamma^1|J^z|\Gamma^1\rangle=-\langle\Gamma^3|J^z|\Gamma^3\rangle$.

J	D^J	Singlet	Triplet	$\bar{\alpha}^2$	$\bar{\beta}$
3	$\Gamma_2\oplus\Gamma_4\oplus\Gamma_5$	Γ_2	Γ_4	0	$\frac{3}{2}$
		Γ_2	Γ_5	4	$\frac{1}{2}$
4	$\Gamma_1\oplus\Gamma_3\oplus\Gamma_4\oplus\Gamma_5$	Γ_1	Γ_4	$\frac{20}{3}$	$\frac{1}{2}$
		Γ_1	Γ_5	0	$\frac{5}{2}$
6	$\Gamma_1\oplus\Gamma_2\oplus\Gamma_3\oplus\Gamma_4\oplus2\Gamma_5$	Γ_1	Γ_4	14	$\frac{1}{2}$
		Γ_1	Γ_5^1	0	$\frac{37}{16}$
		Γ_1	Γ_5^2	0	$\frac{3}{16}$
		Γ_2	Γ_4	0	$\frac{1}{2}$
		Γ_2	Γ_5^1	0	$\frac{37}{16}$
		Γ_2	Γ_5^2	$\frac{45}{4}$	$\frac{3}{16}$
7	$\Gamma_2\oplus\Gamma_3\oplus2\Gamma_4\oplus2\Gamma_5$	Γ_2	Γ_4^1	0	$\frac{35}{16}$
		Γ_2	Γ_4^2	0	$\frac{43}{16}$
		Γ_2	Γ_5^1	$\frac{33}{2}$	$\frac{29}{32}$
		Γ_2	Γ_5^2	$\frac{13}{6}$	$\frac{115}{32}$
8	$\Gamma_1\oplus2\Gamma_3\oplus2\Gamma_4\oplus2\Gamma_5$	Γ_1	Γ_4^1	$\frac{65}{3}$	$\frac{1}{16}$
		Γ_1	Γ_4^2	$\frac{7}{3}$	$\frac{57}{16}$
		Γ_1	Γ_5^1	0	$\frac{51}{32}$
		Γ_1	Γ_5^2	0	$\frac{67}{32}$

solution which we are interested in is guaranteed by $K<0$, $L>0$ which is equivalent to $a<1$. Now, we obtain from (11) that the ferromagnetic order parameter y is equal to zero and the free energy is given by one of the following expressions:

$$f_1=\omega_\alpha^0+\omega_\beta^0+\frac{a}{2c}x^2\ ,$$
$$f_2=\omega_\alpha^0+\omega_\beta^3+\frac{a}{2c}x^2=\omega_\alpha^1+\omega_\beta^0+\frac{a}{2c}x^2\ , \tag{14}$$
$$f_3=\omega_\alpha^1+\omega_\beta^3+\frac{a}{2c}x^2\ .$$

It may be readily shown that other combinations of ω_α and ω_β give higher free-energy values. Let us consider now the conditions for the nonmagnetic ($x=0$) ground state. The function f_1 attains a minimum for $x=0$ only if $b<a$, and in such a case $f_1(0)=0$. The expression for f_2 may be analyzed only numerically and we obtain that $f_2>0$. For $x=2c/a$ we have the minimum of f_3. This function is positive if only $c<a$. In conclusion we obtain the conditions for zero magnetization at $T=0$ K given by the following inequalities:

$$\frac{b}{a}<1,\quad \frac{c}{a}<1\ , \tag{15}$$

analogously to those of Kitano and Trammell[1] for the ferromagnetic case ($A<1$, $B<1$).

The condition for occurrence of the antiferromagnetic ordering at finite temperatures can be obtained from the expansion of the free energy, Eq. (5), in terms of the antiferromagnetic order parameter x:

$$f=F_0+F_2(t)x^2+\cdots\ . \tag{16}$$

If F_2 becomes negative in a certain temperature region a nonzero value of x minimizes the free energy. It is possible to calculate F_2 explicitly at the temperature where this function attains its minimal value. Consequently the condition for the heat ordering is given as follows:

$$F_2(t_{\min})<0\ , \tag{17}$$

which yields the inequality

$$-4\ln\left[\frac{4c}{a-b}\right]+\frac{3a+b+4c}{c}<0\ . \tag{18}$$

This requirement has again the same form as that obtained by Kitano and Trammell,[1] for the ferromagnetic case, if we identify b/a and c/a with their A and B, respectively.

IV. *t-h* PHASE DIAGRAMS

The results which are qualitatively new in comparison with the ferromagnetic case are obtained if we plot the phase diagrams in the temperature–magnetic-field plane. This requires laborious numerical analysis of the self-consistent equations for the order parameters Eq. (11) and for the free energy Eq. (5). A series of the phase diagrams is shown in Fig. 1 for increasing value of the pa-

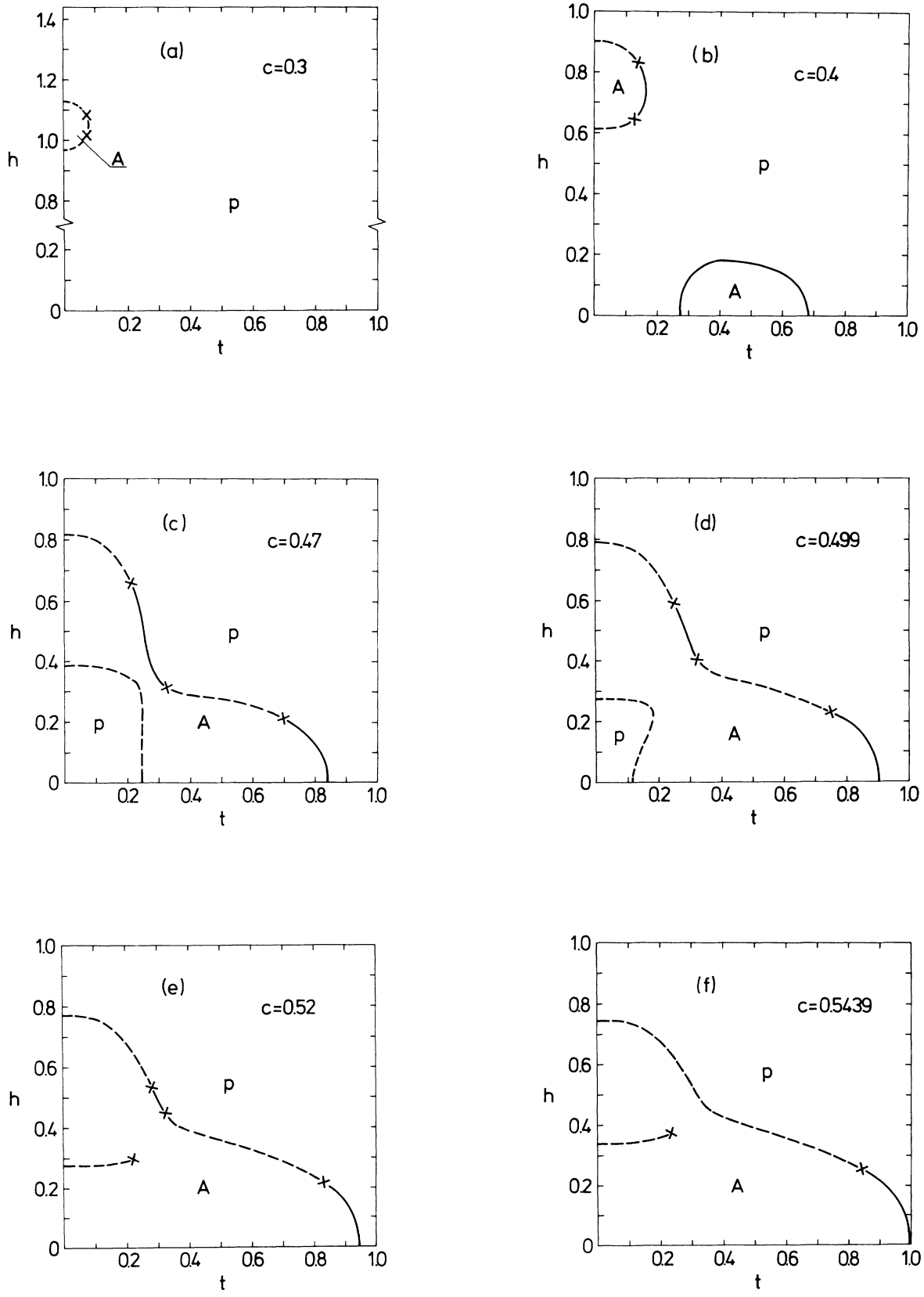

FIG. 1. Magnetic phase diagrams for the parameters $a=0.5$, $b=0.4$, and different values of c. A is the antiferromagnetic phase, P the paramagnetic phase. The dashed and solid lines denote discontinuous and continuous transitions, respectively. The crosses on the upper phase boundary denote the tricritical points while the cross within the A phase marks the critical endpoint.

rameter c [see Eq. (8)]. The series begins with the case when there is no ordering in absence of the magnetic field, i.e., the first condition (15) for the heat ordering is fulfilled while the second (18) is not. The field-ordered region is bounded by a line of first- and second-order phase transitions separated by the two tricritical points. If both conditions (15) and (18) are satisfied, heat ordering appears [Fig. 1(b)]. The regions of heat and field ordering join together in Fig. 1(c) dividing the paramagnetic phase into two separate domains. The upper phase boundary includes now three tricritical points. It is interesting to point out that for $T=0$ it is possible to distinguish between the low- and high-field paramagnetic phases. In the first case the lowest-lying energy levels are ω_α^0 and ω_β^0 while for the second case they are ω_α^1 and ω_β^1. This difference vanishes at higher temperatures where all the levels contribute to the free energy simultaneously.

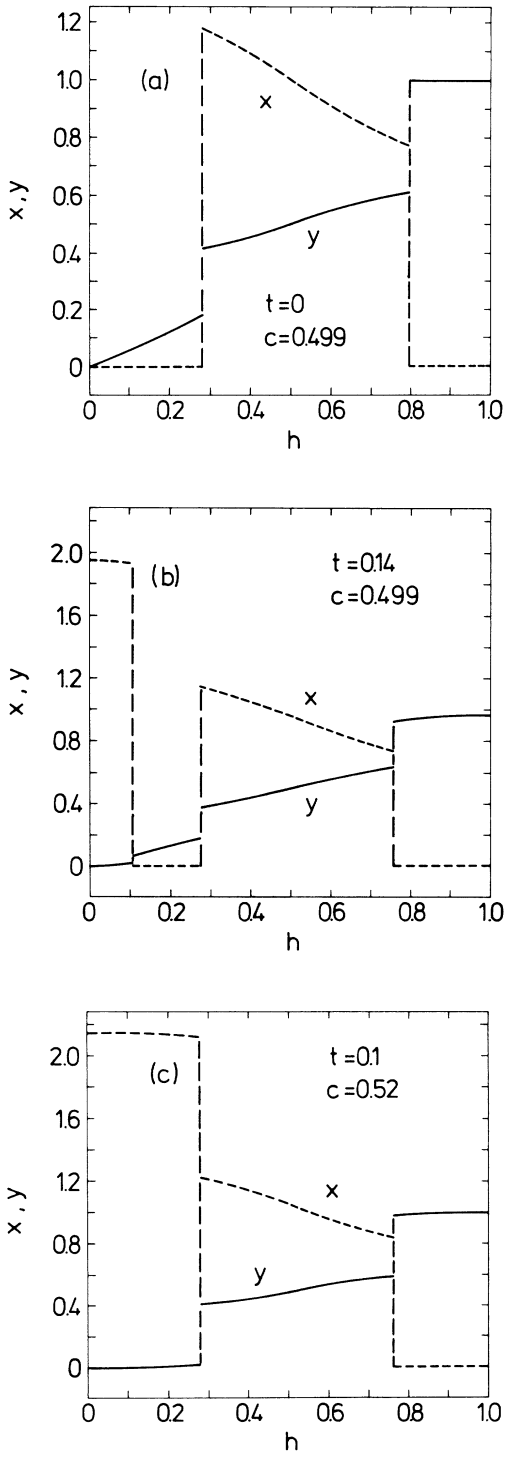

FIG. 2. Antiferromagnetic order parameter x and the magnetization y vs magnetic field for $a=0.5$ and $b=0.4$.

The process of heat ordering can be either continuous Fig. 1(b), or discontinuous Fig. 1(c) as was the case for the ferromagnetic solution of the model considered here.

Along the isotherms corresponding to the diagram in Fig. 1(d) we plotted the order parameters as a function of magnetic field for two different values of temperature [Figs. 2(a) and 2(b)]. Therefore, we obtained the two- and three-threshold reentrant transitions to the paramagnetic phase as well as the reentrance to the antiferromagnetic phase [Fig. 2(b)].

For $c>0.5$ there is no heat ordering, and the low-field and low-temperature paramagnetic phase vanishes [Fig. 1(e)], but inside the antiferromagnetic phase there appears a line of discontinuous phase transitions terminating at the critical endpoint. The order parameters have a jump along this line as shown in Fig. 2(c). We then conclude that the crystal field can produce something very similar to a spin-flop transition.

For higher values of the parameter c, Fig. 1(f), the number of tricritical points at the upper phase boundary is reduced from three to one.

We should point out that the phase diagrams derived in this work and even the order of the phase transitions may change if better statistical-mechanics approximations going beyond the mean-field approximation are applied.

It is also of interest to consider the effects of Heisenberg antiferromagnetic exchange (this work is in progress) as far as the phase diagrams and the collective excitations are concerned.

V. CONCLUSIONS

Searching for the possibilities of heat ordering in the singlet-triplet model with antiferromagnetic intersublattice coupling described by the Ising Hamiltonian, we have found the conditions for this phenomenon to occur. They are formally analogous to those obtained by Kitano and Trammell[1] for the ferromagnetic case. We have shown that the phase transition from the low-temperature paramagnetic phase to the high-temperature antiferromagnetic phase can be either continuous or discontinuous, as might be expected from our previous investigations.[3] Moreover, essentially new reentrant transitions are found. We have obtained reentrance to the paramagnetic phase when the magnetic field or the temperature increase as well as to the antiferromagnetic phase when the magnetic field increases [Fig. 1(d)].

The present model of the heat magnetization is a relatively simple one and a direct comparison with experi-

ment might be no easy matter. However, the diagram in Fig. 1(f) may be considered as a simplified version of the case of the rare-earth antimonide HoSb. As has been reported earlier[6] the parameter x which gives the ratio of the fourth-order to the sixth-order cubic anisotropy is close to $\frac{6}{7}$ for this compound. According to Lea *et al.*[7] for $x > \frac{6}{7}$ the lowest-lying states of Ho^{3+} are Γ_1 and Γ_4^2 which suggests the singlet-triplet model to be applicable here if we neglect the low-lying doublet Γ_3. As it may be seen from Table I for $J=8$ and for the Γ_1, Γ_4^2 scheme one has $c/b=\bar{\beta}^2/(4\bar{\alpha}^2)=1.3598$ which is really the case of the diagram shown in Fig. 1(f). This diagram reflects one important feature of HoSb, e.g., the two successive phase transitions with increasing magnetic field at a low temperature, which is shown more exactly in Fig. 2(c).

More detailed theories of HoSb (Refs. 6 and 8) take into account also the doublet Γ_3 and include isotropic bilinear pair interactions as well as the quadrupolar pair couplings. These models are able to describe most of the magnetic properties of HoSb, especially the unusual tricritical-like behavior and a rotation of magnetic moments in intermediate external fields.[6,9]

Finally let us stress that it would also be interesting to find the experimental evidences for the phase diagrams shown in Figs. 1(a)–1(e). However, the intrinsic richness of the model presented as far as the field- and temperature-induced phase transitions are concerned makes it worth further theoretical studies.

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*On leave of absence from Institute of Physics, A. Mickiewicz University, PL-60-769 Poznań, Poland.

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