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Theory of Phase Transitions in Rare-Earth Vanadates[†]

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The crystallographic and magnetic phase transitions in the rare-earth vanadates $TmVO_4$, $DyVO_4$, and $TbVO_4$ are studied. Symmetry-adapted spin Hamiltonians, involving quadrupolar and dipolar interactions, are constructed and treated in the molecular-field approximation. The competition between Jahn–Teller distortion and magnetic ordering is illustrated by the comparison of $TmVO_4$ and $TbPO_4$. The two phase transitions found in $DyVO_4$ are reproduced and it is shown that a dipolar phase transition might appear in $TbVO_4$ at a very low temperature. We also determine the influence of a magnetic field applied along the various symmetry axes.

I. INTRODUCTION

Rare-earth vanadates (and also phosphates and arsenates) display an interesting variety of crystallographic and magnetic phase transitions. For instance, $DyVO_4$ [1] undergoes a crystallographic phase transition at 14 °K in which the symmetry is lowered from that of the tetragonal zircon structure (D_{4h}^{19}) to the orthorhombic symmetry D_{2h}^{28}; antiferromagnetic ordering appears below 3 °K, with the ordering axis along the *a* or *b* axis of the tetragonal cell. $TbVO_4$ [2] and $TmVO_4$ [3] undergo only a crystallographic phase transition, at 33 and 2.3 °K, respectively, in which the symmetry is lowered to D_{2h}^{24}.

In Ref. 4 it has been shown that magnetic systems with dipolar and quadrupolar interactions may show two successive phase transitions: A quadrupolar phase transition followed, at a lower temperature, by an ordinary dipolar magnetic phase transition. Although only Ising-like interactions were introduced, the theory gave a good qualitative picture of the magnetic properties of $DyVO_4$. However, quadrupolar ordering in $DyVO_4$ is nonaxial, and dipolar ordering appears in the basal plane.

In this paper, a similar theory is presented and applied to $TmVO_4$, $DyVO_4$, and $TbVO_4$. More realistic interactions are introduced: nonaxial quadrupolar interactions,[5] in-plane dipolar interactions, an axial crystalline field, and Zeeman interactions along the symmetry axis. Similar molecular-field calculations have already been performed by Pytte and Stevens.[6] These authors considered only the crystallographic phase transition; their order parameter is a lattice distortion whose value is determined self-consistently. This lattice model and the present author's molecular-field treatment of an interacting system are equivalent.[7] In the author's formalism, only the spin system is considered; magnetic as well as crystallographic phase transitions can be described, and the influence of a magnetic field on the crystallographic phase transition is easily studied. This treatment is purely phenomenological and the origin of the various dipolar and quadrupolar phase transitions are not discussed, as Pytte and Stevens did. Elliott *et al.*[8] have also presented a molecular-field treatment of the crystallographic phase transition in $DyVO_4$. They considered the coupling of the Dy^{3+} ion to both the dynamic phonon modes and to the static elastic strain and they solved the coupled equations of motion for the long-wavelength acoustic phonons.

This paper is organized as follows. In Sec. II the spin Hamiltonian adapted to each compound is determined, using simple group-theoretical arguments. In Sec. III the elementary case of $TmVO_4$ is considered. In Secs. IV and V, respectively, the phase transitions in $DyVO_4$ and $TbVO_4$ are described. It is shown in particular that the application of a magnetic field along the *c* axis can suppress the orthorhombic distortion, and that a dipolar phase transition might appear in $TbVO_4$ below 1 °K.

II. SPIN HAMILTONIAN

The three ions Tm^{3+}, Dy^{3+}, and Tb^{3+} in rare-earth vanadates have low-lying crystalline field levels well separated from the excited levels: a non-Kramers doublet Γ_5 for Tm^{3+} [9]; two Kramers doublets Γ_6 and Γ_7 for Dy^{3+} [1], two singlets Γ_1 and Γ_3, and a doublet Γ_5 for Tb^{3+}.[2] In the following, we shall neglect entirely the other excited states and describe each ion by a spin Hamiltonian. We need to know the form of the operators S^x, S^y, S^z, $(S^z)^2 - \frac{1}{3}S(S+1)$, $(S^x)^2-(S^y)^2$, and $S^xS^y+S^yS^x$. The transformation properties of these operators under the operations of the point group $D_{2d} \equiv \bar{4}2m$ are shown in Table I (*x* and *y* are chosen along the *a* and *b* axes of the tetragonal cell).

Tm^{3+}

Since $\Gamma_5^2 = \Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$, $\langle\Gamma_5|S^x|\Gamma_5\rangle = 0$, $\langle\Gamma_5|S^y|\Gamma_5\rangle = 0$, and $\langle\Gamma_5|S^z|\Gamma_5\rangle \neq 0$, we may then

TABLE I. Transformation properties of the dipolar and quadrupolar operators in group $D_{2d}=\bar{4}2m$.

Γ_1	A_{1g}		$(S^x)^2+(S^y)^2;\ (S^z)^2$
Γ_2	A_{2g}	S_z	
Γ_3	$B1_g$		$(S^x)^2-(S^y)^2$
Γ_4	B_{2g}		$S^xS^y+S^yS^x$
Γ_5	E_g	$\begin{pmatrix} S^x \\ S^y \end{pmatrix}$	$\begin{pmatrix} S^yS^z+S^zS^y \\ -S^xS^z-S^zS^x \end{pmatrix}$

write

$$S^z=g_z\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} .$$

$\langle\Gamma_5\,|\,(S^z)^2-\frac{1}{3}S(S+1)\,|\,\Gamma_5\rangle$ is different from zero, and in the eigenbasis of S^z,

$$(S^z)^2-\tfrac{1}{3}S(S+1)=\tfrac{1}{2}Q_0\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} .$$

Q_0 is the average of $(S^z)^2-\frac{1}{3}S(S+1)$ above the transition temperature. We look for the operator $S^xS^y+S^yS^x$ whose average measures an orthorhombic distortion along [110]. This operator depends on one parameter, since Γ_4 appears only once in Γ_5^2, and is nondiagonal in the eigenbasis of S^z since the eigenfunctions of S^z have an axial symmetry, so that we may take

$$S^xS^y+S^yS^x=\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} .$$

Dy^{3+}

Since $\Gamma_6^2=\Gamma_7^2=\Gamma_1+\Gamma_2+\Gamma_5$ and $\Gamma_6\Gamma_7=\Gamma_3+\Gamma_4+\Gamma_5$, we have

$$S^z=\begin{array}{c} \begin{array}{cc} \Gamma_6 & \Gamma_7 \end{array} \\ \begin{pmatrix} g_6 & & & \\ & -g_6 & & \\ & & g_7 & \\ & & & -g_7 \end{pmatrix} \end{array} \begin{array}{l} \Gamma_6 \\ \\ \Gamma_7 \end{array} .$$

In the same basis

$$(S^z)^2-\frac{S(S+1)}{3}=\begin{pmatrix} q_6 & & & \\ & q_6 & & \\ & & q_7 & \\ & & & q_7 \end{pmatrix} ,$$

with $\frac{1}{4}(2q_6+2q_7)=Q_0$. We look for S^x, which depends on three parameters, and $(S^x)^2-(S^y)^2$, which depends only on one parameter. We may take

$$S^x=\begin{pmatrix} & a & & c \\ -a & & c & \\ & c & & b \\ c & & -b & \end{pmatrix}$$

and

$$(S^x)^2-(S^y)^2=\begin{pmatrix} & & & 1 \\ & & 1 & \\ & 1 & & \\ 1 & & & \end{pmatrix} .$$

Tb^{3+}

Since $\Gamma_1^2=\Gamma_3^3=\Gamma_1$, $\Gamma_1\Gamma_3=\Gamma_3$, $\Gamma_1\Gamma_5=\Gamma_3\Gamma_5=\Gamma_5$, and $\Gamma_5^2=\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$, then S^z, $(S^z)^2-\frac{1}{3}S(S+1)$, S^x, and $S^xS^y+S^yS^x$ depend, respectively, on 1, 1, 2, and 1 parameters:

$$S^z=\begin{array}{c} \begin{array}{ccc} \Gamma_3 & \Gamma_5 & \Gamma_1 \end{array} \\ \begin{pmatrix} 0 & & & \\ & g_5 & & \\ & & -g_5 & \\ & & & 0 \end{pmatrix} \end{array} \begin{array}{l} \Gamma_3 \\ \Gamma_5 \\ \\ \Gamma_1 \end{array} , \qquad (S^z)^2-\frac{S(S+1)}{3}=\begin{pmatrix} q_3 & & & \\ & q_5 & & \\ & & q_5 & \\ & & & q_1 \end{pmatrix} ,$$

$$S^{\substack{x\\y}}=\begin{pmatrix} & g_{35} & \pm g_{35} & \\ g_{35} & & & g_{15} \\ \pm g_{35} & & & \pm g_{15} \\ & g_{15} & \pm g_{15} & \end{pmatrix} , \qquad S^xS^y+S^yS^x=\begin{pmatrix} & & & p_{13} \\ & & p_{55} & \\ & p_{55} & & \\ p_{13} & & & \end{pmatrix} .$$

We shall write later $S^xS^y+S^yS^x=p_{13}P_{13}+p_{55}P_{55}$ and $S^x=g_{15}S_{15}+g_{35}S_{35}$.

As explained in the Appendix, it is possible to describe the crystal field band $(\Gamma_1+\Gamma_5+\Gamma_3)$ of Tb^{3+} using two effective spins $\frac{1}{2}$, $\vec{\sigma}$ and $\vec{\tau}$.[10] In the following, however, we shall not use the expressions of

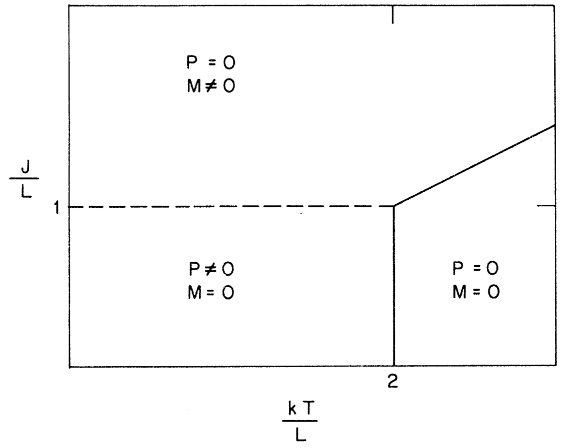

FIG. 1. Competition between dipolar and quadrupolar ordering when the ground crystalline level is Γ_5 ($TmVO_4$ and $TbPO_4$).

the dipolar and quadrupolar operators as a function of $\vec{\sigma}$ and $\vec{\tau}$.

III. PHASE TRANSITION IN $TmVO_4$

We consider the following Hamiltonian $\mathcal{H}$ for a lattice of spins $S' = \frac{1}{2}$, and the corresponding molecular-field Hamiltonian $\mathcal{H}_0$ (we choose $g_z = 1$ to simplify the notations):

$$\mathcal{H} = -\sum_{i,j} J_{ij} S_i^z S_j^z - \sum_{i,j} L_{ij} P_i P_j \ , \tag{1}$$

$$\mathcal{H}_0 / N = -H S_i^z - \eta P_i \ . \tag{2}$$

$P_i = S_i^x S_i^y + S_i^y S_i^x$. H and η are the molecular fields associated with the order parameters $M = \langle S_i^z \rangle$ and $P = \langle P_i \rangle$. The choice of the nonaxial quadrupolar parameter [$S^x S^y + S^x S^y$, and not $(S^x)^2 - (S^y)^2$ or a linear combination of these two operators] allows only distortions along [110], as observed experimentally. This procedure, although not general, avoids the introduction of a fourth-order anisotropy in the a-b plane.

Following the method used in Ref. 4, we easily get $H = 2JM$ and $\eta = 2LP$, whence the two self-consistent equations for M and P:

$$M = 2JM(\tanh\beta\lambda)/\lambda \ , \tag{3}$$

$$P = 2LP(\tanh\beta\lambda)/\lambda \ , \tag{4}$$

with

$$\lambda^2 = 4J^2M^2 + 4L^2P^2 \ . \tag{5}$$

J and K are the Fourier transforms of the interactions J_{ij} and K_{ij}; for instance, $J \equiv J(0) = \sum_j J_{ij}$.

The phase diagram in the (kT/L, J/L) plane is shown in Fig. 1. There is either dipolar or quadrupolar ordering (except for $J = L$, in which case the ratio M/P is not determined) and the transition is second order. The first situation corresponds approximately to $TbVO_4$.[11] The second situation is found in $TmVO_4$[3] and $TmAsO_4$.[12] The ground crystalline level of Ho^{3+} in $HoPO_4$ is Γ_5,[13] but no phase transition in $HoPO_4$ has been reported yet.

Suppose now $J = 0$. A magnetic field along the c axis stabilizes the quadratic phase[3,12] (in the distorted phase, $\Gamma_5 \rightarrow \Gamma_2 + \Gamma_4$, $\langle \Gamma_2 | S^z | \Gamma_4 \rangle \neq 0$). The Hamiltonian of the system is similar to that of an $S' = \frac{1}{2}$ Ising dipolar system in a transverse field[14] and in fact the operators P and $(S^x)'$ are identical; if $H_z \neq 0$, there is a distortion only if L is larger than a threshold value proportional to H_z. A field in the a-b plane has no effect on the distortion since $\langle \Gamma_5 | S^x | \Gamma_5 \rangle = \langle \Gamma_5 | S^y | \Gamma_5 \rangle = 0$.

IV. PHASE TRANSITIONS IN $DyVO_4$

Because of the lack of experimental information and in order to simplify the problem, we shall use the following values for the parameters of the spin Hamiltonian:

$$g_6 = \tfrac{1}{2} \ , \qquad g_7 = \tfrac{3}{2} \ ,$$

$$q_6 = -1 \ , \qquad q_7 = +1 \ ,$$

$$a = b = \tfrac{1}{2}\sqrt{3} \ , \qquad c = 1 \ ,$$

which means using a true spin $\frac{3}{2}$ to describe the levels $\Gamma_6 (S^z = \pm\frac{1}{2})$ and $\Gamma_7 (S^z = \pm\frac{3}{2})$ of the Dy^{3+} ion. We shall consider first the following quadrupolar Hamiltonian ($D > 0$):

$$\mathcal{H} = D\sum_i Q_i - \sum_{i,j} K_{ij} Q_i Q_j - \sum_{i,j} L_{ij} P_i P_j \ , \tag{6}$$

with

$$Q_i = (S_i^z)^2 - \tfrac{1}{3} S(S+1) \ ,$$

$$P_i = (S_i^x)^2 - (S_i^y)^2 \ .$$

We restrict ourselves to positive values of $K = K(0) = \sum_j J_{ij}$ and $L = L(0) = \sum_j L_{ij}$. If $L/K = \frac{1}{3}$ and $D = 0$ only, $\mathcal{H}$ is isotropic.[5]

If σ and η are the molecular fields associated to the order parameters $Q = \langle Q_i \rangle$ and $P = \langle P_i \rangle$ the molecular-field Hamiltonian is

$$\mathcal{H}_0 / N = (D - \sigma) Q_i - \eta P_i \ . \tag{7}$$

The molecular-field equations are $\sigma = 2KQ$ and $\eta = 2LP$, whence the self-consistency relations for Q and P:

$$Q = (2KQ - D)(\tanh\beta\lambda)/\lambda \ , \tag{8}$$

$$P = 6LP(\tanh\beta\lambda)/\lambda \ , \tag{9}$$

with

$$\lambda^2 = (D - 2KQ)^2 + 12L^2P^2 \ . \tag{10}$$

The free energy per ion is given by

$$\phi_0 / N = -(1/\beta)\ln(4\cosh\beta\lambda) + KQ^2 + LP^2 \ . \tag{11}$$

A first solution of the coupled equations (8)–(10)

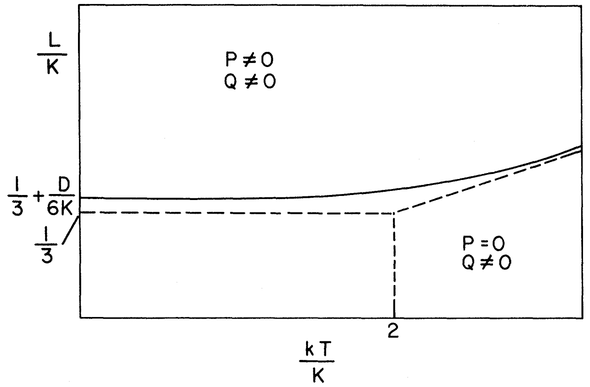

FIG. 2. Axial and nonaxial ordering in $DyVO_4$; the phase diagram in the $(kT/K,\ L/K)$ plane is shown for $D=0$ (dashed lines) and $D=0.3$ (full line).

is $P=0$, $Q=\tanh[\beta(2KQ-D)]$. It describes an axial phase. A second solution describes an orthorhombic phase (the sign of P is not determined, $P>0$ and $P<0$ describe two domains $a/b>1$ and $a/b<1$):

$$Q=Q_0=D/(2K-6L)\,, \qquad (12a)$$

$$P^2=\lambda^2/12L^2-3Q_0^2\,, \qquad (12b)$$

$$\lambda=6L\tanh\beta\lambda\,. \qquad (12c)$$

At 0 °K, $\lambda=6L$ and $P=\sqrt{3}(1-Q_0^2)^{1/2}$. The condition $|Q_0|\leq 1$ gives the stability condition of the orthorhombic phase

$$L>\tfrac{1}{3}K+\tfrac{1}{6}D\,. \qquad (13)$$

If this condition is fulfilled, the transition in P is second order; the transition temperature T_p ($\beta_p=1/kT_p$) is given by

$$Q_0=\tanh 6\beta_p LQ_0\,.$$

The phase diagram in the $(kT/K,\ L/K)$ plane is shown in Fig. 2. For $D=0$ (dashed lines) there is a phase transition either in $Q(L<\frac{1}{3}K)$ or in $P(L>\frac{1}{3}K)$ (if $L=\frac{1}{3}K$ only P^2+3Q^2 is determined as a function of T). For $D\neq 0$, the second-order transition in Q disappears; if $L\gg D$, K one has $kT_P\simeq 6L$.

In $DyVO_4$,[1] $kT_P=14$ °K and $2D=3\ \mathrm{cm}^{-1}\simeq 4.5$ °K so that if $K=0$, $L=2.35$ °K (if $2D=9\ \mathrm{cm}^{-1}$, $L=2.5$ °K). Figure 3 represents the phase diagram for $K=0$, Fig. 4 the thermal variation of P and Q (full lines); $Q_0=-0.16$ and $P_0=1.71$. Since the only experimental result is the value of T_p, it is not possible to evaluate L and K independently. (The splitting between the two Kramers doublets near the saturation is known experimentally, but is not independent of T_p in the molecular-field approximation; we have chosen to fit L to the value of T_p.)

Equations (8)–(10) are very similar to the molecular-field equations for an Ising model in a perpendicular field.[14] In the two problems, a threshold value of the interaction between ions is found. Here the axial crystalline field opposes an orthorhombic distortion, and such a distortion is stable only if it can lower the energy of the ground state. The same situation is found in the problem of magnetic ordering among non-Kramers ions whose single-ion ground state is made of two nonmagnetic singlets.[15]

A magnetic field H_z along the c axis stabilizes the axial phase. The threshold value for L is increased as shown in Fig. 3 (dashed line) for $H_z=10$ °K (in practice a large field would be necessary to lower the transition in P since the spectroscopic g_6 and g_7 factors of $DyVO_4$ are very small). Figure 4 shows the thermal variation of P, Q, and $M_z=\langle S^z\rangle$ for $H_z=10$ °K. Q is no longer a constant below T_p and may be positive. The saturation value of P is decreased by H_z; the saturation of M_z is opposed by the distortion, whence the plateau of $M_z(T)$ around T_P.

A magnetic field H_x along the a axis suppresses the second-order transition in P as shown in Fig.

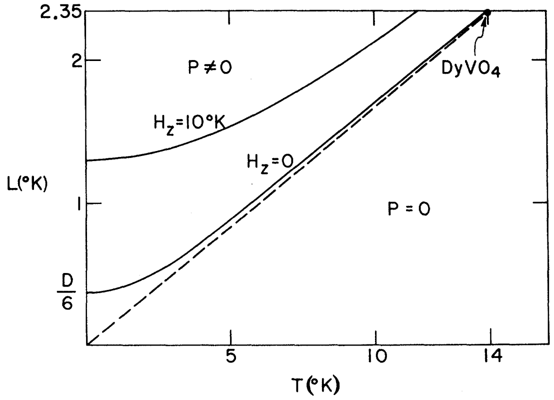

FIG. 3. Phase diagram in the $(T,\ L)$ plane for $DyVO_4$; $K=0$, $D=2.25$ °K; $H_z=0$ and $H_z=10$ °K. The dashed line corresponds to $D=0$ and $H_z=0$.

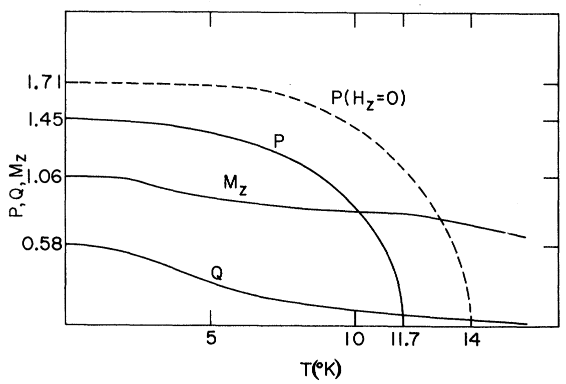

FIG. 4. Thermal variation of P, Q, and M_z in $DyVO_4$ for $H_z=10$ °K. The dashed line represents the thermal variation of P for $H_z=0$.

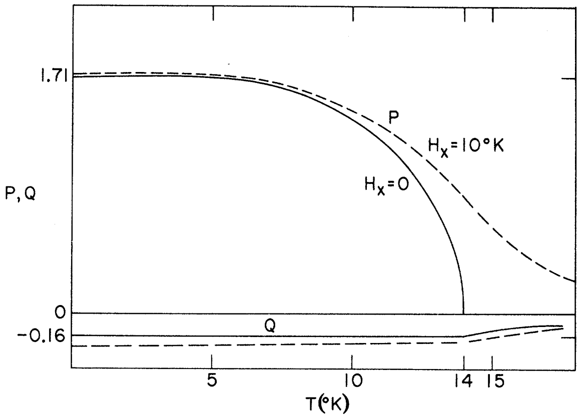

FIG. 5. Thermal variation of P and Q in DyVO$_4$; $H_x=0$ (full lines) and $H_x=5$ °K (dashed lines).

5 (dashed line) since it induces a deformation of the quadrupoles in the basal plane already at high temperature. Moreover, the field H_x favors the domains with $P>0$, and the saturation value of P is increased slightly. Similarly, a field H_y favors the domains with $P<0$.

Dipolar Ordering

We now add to the quadrupolar Hamiltonian (6) an X-Y dipolar Hamiltonian

$$\mathcal{H}_{\rm dip} = -\sum_{i,j} J_{ij}(S_i^x S_j^x + S_i^y S_j^y) . \tag{14}$$

We neglect dipolar interactions of the z components of the moments since at low temperature the moments are mainly in the a-b plane.[6] We first suppose that $J \equiv J(0) = \sum_j J_{ij}$ is positive (as long as no external field along a or b is introduced, the sign of J is not important). We look for the possibility of ordering in the three parameters $P = \langle (S_i^x)^2 - (S_i^y)^2 \rangle$, $M_x = \langle S_i^x \rangle$, and $M_y = \langle S_i^y \rangle$. The molecular-field Hamiltonian is

$$\mathcal{H}_0/N = DQ_i - \eta P_i - H_x S_i^x - H_y S_i^y . \tag{15}$$

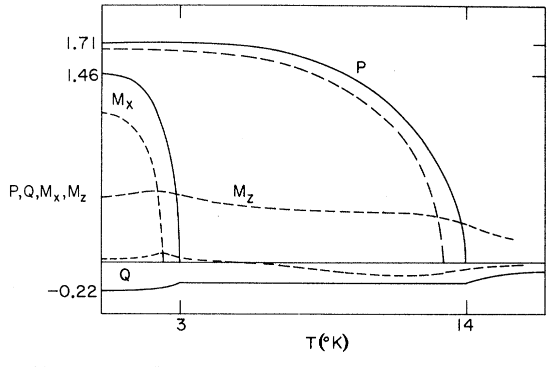

FIG. 6. Dipolar and quadrupolar ordering in DyVO$_4$; $L=2.35$ °K; $J=0.72$ °K ($T_{M_x}=3$ °K, $T_p=14$ °K). The dashed lines correspond to $H_z=5$ °K.

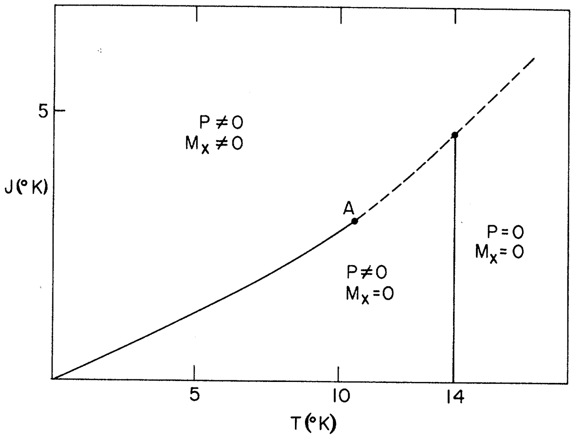

FIG. 7. Phase diagram in the (T, J) plane for DyVO$_4$, $L=2.35$ °K. The dashed line represents first-order transitions, A is a tricritical point. For large values of J, the transition becomes second order.

The molecular fields are given by $H_x = 2JM_x$, $H_y = 2JM_y$, and $\eta = 2LP$, whence the self-consistent equations

$$M_x = \langle S_i^x \rangle_0, \quad M_y = \langle S_i^y \rangle_0, \quad P = \langle P_i \rangle_0 \tag{16}$$

and the free energy

$$\phi_0/N = -(1/\beta)\ln Z_0 + J(M_x^2 + M_y^2) + LP^2 . \tag{17}$$

One finds that if $M_x \neq 0$, $M_y = 0$ and $P>0$.

For $L=2.35$ and $J=0.72$ two successive second-order phase transitions in P and M_x (or M_y) are found, as shown in Fig. 6 (full lines). For larger values of J/L, only one phase transition is found; it may be first or second order (Fig. 7). The saturation value of M_x is slightly less than $\frac{3}{2}$ because $D \neq 0$, and Q is no longer constant below T_{M_x}. In fact, the ground-state doublet of the system is at 0 °K:

$$0.46\, |\pm\tfrac{3}{2}\rangle + 0.54\, |\mp\tfrac{1}{2}\rangle$$

in the absence of dipolar interactions ($Q=-0.16$ at $T=0$ °K) and

$$0.445(|\tfrac{3}{2}\rangle + |-\tfrac{3}{2}\rangle) + 0.55(|\tfrac{1}{2}\rangle + |-\tfrac{1}{2}\rangle) ,$$

when $J=0.72$ ($Q=-0.21$ at $T=0$ °K).

An external field H_z lowers both T_{M_x} and T_p, as Fig. 6 shows. In larger fields, the dipolar transition, then the quadrupolar transition, are suppressed. An external field along x suppresses the two transitions. Figure 8 shows the successive splittings of the quadruplet $S=\frac{3}{2}$ by dipolar and quadrupolar interactions.

Remark

In the preceding calculations, it is convenient to quantize along the x axis, so that all matrices are real if no external H_z field is applied. In the

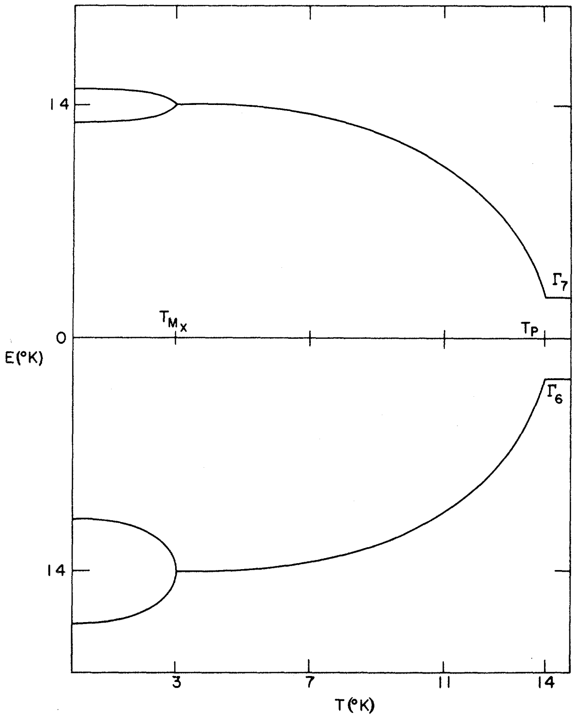

FIG. 8. Splitting of the quadruplet $S=\frac{3}{2}$ by dipolar and quadrupolar interactions in $DyVO_4$.

low-temperature phase, the eigenstates are almost $|\pm\frac{3}{2}\rangle$, $|\pm\frac{1}{2}\rangle$; in the quadrupolar phase, $(1/\sqrt{2})(|\frac{3}{2}\rangle \pm |-\frac{3}{2}\rangle)$ and $(1/\sqrt{2})(|\frac{1}{2}\rangle \pm |-\frac{1}{2}\rangle)$, and in the disordered phase

$$0.87\,|\pm\tfrac{3}{2}\rangle + 0.50\,|\mp\tfrac{1}{2}\rangle$$

and

$$0.50\,|\pm\tfrac{3}{2}\rangle - 0.87\,|\mp\tfrac{1}{2}\rangle\ .$$

We consider now antiferromagnetic dipolar interactions. In a zero external field along x, the phase diagrams for $J>0$ and $J<0$ are the same. When a low field H_x is applied, the magnetic structure remains antiferromagnetic; the transition at T_P is suppressed and T_{M_x} is decreased.

Below T_{M_x}, H_x connects the two doublets, as is obvious from the above remark, but since the splitting between these doublets is large compared to J and H_x, the system is almost Ising like.[16] Figure 9 shows the phase diagram in the (T, H_x) plane. A spin-flop phase would appear only if the quadrupolar interactions were much weaker.

V. PHASE TRANSITIONS IN $TbVO_4$

We consider first the following quadrupolar Hamiltonian and the corresponding molecular-field Hamiltonian:

$$\mathcal{H} = N\mathcal{H}_c - \sum_{i,j} L_{ij} P_i P_j\ , \tag{18}$$

$$\mathcal{H}_0/N = \mathcal{H}_c - H_{13}P_{13} - H_{55}P_{55}\ . \tag{19}$$

$\mathcal{H}_c$, P_{13}, and P_{55} have been defined in Sec. II. P_{13} and P_{55} are two independent operators, so that two molecular fields H_{13} and H_{55} must be introduced. Of course since the quadrupolar transition in $TbVO_4$ is characterized by a single-order parameter $P=p_{13}\langle P_{13}\rangle + p_{55}\langle P_{55}\rangle$, the two molecular fields are not independent; both are related to the value of the orthorhombic distortion. H_{13} describes the separation of the levels Γ_1 and Γ_3, H_{55} the splitting of the level Γ_5:

$$\mathcal{H}_0 = \begin{pmatrix} \Delta_3 & & & -H_{13} \\ & & -H_{55} & \\ & -H_{55} & & \\ -H_{13} & & & -\Delta_1 \end{pmatrix}\ ,$$

with $\Delta^{\pm} = \frac{1}{2}(\Delta_1 \pm \Delta_3)$, the eigenvalues of $\mathcal{H}_0$ are H_{55} and $\lambda = \Delta^- \pm R$, $R^2 = \Delta^{+2} + H_{13}^2$. We now have

$$Z_0 = 2\cosh\beta H_{55} + 2\,e^{-\beta\Delta^-}\cosh\beta R\ , \tag{20a}$$

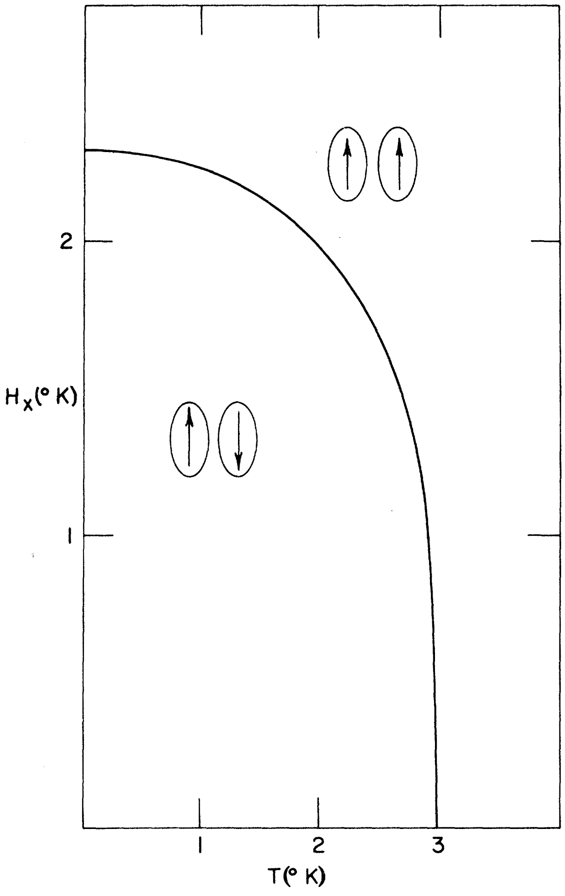

FIG. 9. Phase diagram of $DyVO_4$ in the (T, H_x) plane for $J=-0.72$ °K.

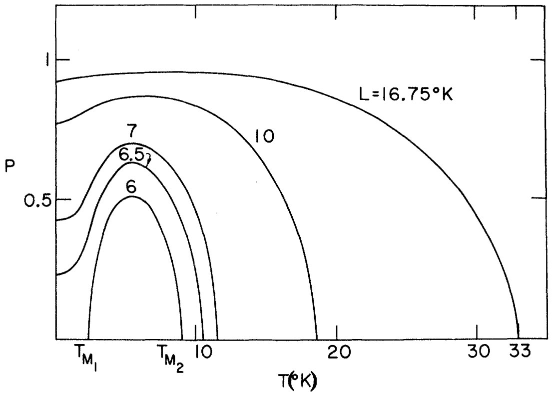

FIG. 10. Thermal variations of the order parameter P in $TbVO_4$ for various values of the interaction L.

$$Z_0\langle P_{13}\rangle = 2\,e^{-\beta\Delta^-}H_{13}\,(\sinh\beta R)/R\ , \tag{20b}$$

$$Z_0\langle P_{55}\rangle = 2\sinh\beta H_{55}\ , \tag{20c}$$

$$\phi_0 = -\,(1/\beta)\ln Z_0 + H_{13}\langle P_{13}\rangle + H_{55}\langle P_{55}\rangle - L(p_{13}\langle P_{13}\rangle + p_{55}\langle P_{55}\rangle)^2\ . \tag{21}$$

The conditions $\partial\phi_0/\partial H_{13} = \partial\phi_0/\partial H_{55} = 0$ give

$$H_{13} = 2p_{13}LP\ , \tag{22a}$$

$$H_{55} = 2p_{55}LP\ , \tag{22b}$$

whence

$$\phi_0 = -\,(1/\beta)\ln Z_0 + LP^2\ , \tag{23a}$$

$$Z_0 = 2\cosh 2\beta p_{55}LP + 2\,e^{-\beta\Delta^-}\cosh\beta R\ , \tag{23b}$$

$$R^2 = \Delta^{+2} + (2p_{13}LP)^2\ , \tag{23c}$$

$$Z_0P = 4p_{13}^2LPe^{-\beta\Delta^-}(\sinh\beta R)/R + 2p_{55}\sinh 2\beta p_{55}LP\ . \tag{23d}$$

The temperature of the transition in P, which is second order, is given by

$$2 + 2\,e^{-\beta\Delta^-}\cosh\beta\Delta^+ = 4p_{13}^2\,Le^{-\beta\Delta^-}(\sinh\beta\Delta^+)/\Delta^+ + 4\beta p_{55}^2L\ , \tag{24}$$

which gives for $kT_M \gg \Delta_1,\ \Delta_3$:

$$kT_p = (p_{13}^2 + p_{55}^2)\,L\ . \tag{25}$$

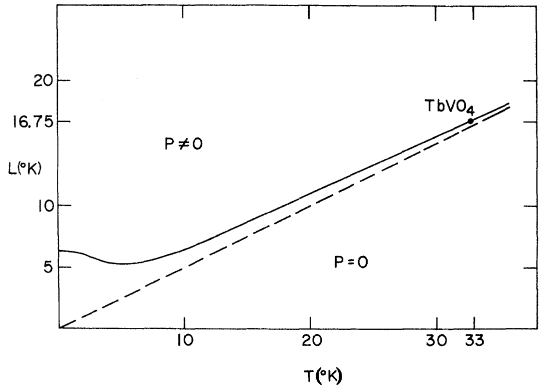

FIG. 11. Quadrupolar transition in $TbVO_4$; phase diagram in the $(T,\ L)$ plane. The dashed line corresponds to $\Delta_1 = \Delta_3 = 0$.

Figure 10 shows the thermal variation of the order parameter P for various values of L ($T_p = 33$ °K for $L = 16.75$ °K) supposing $p_{13} = p_{55} = 1$. Figure 11 shows the phase diagram in the (T, L) plane; for low values of L, there is no phase transition; for $5.2 < L < 6.3$ there are two second-order phase transitions at T_{M1} and T_{M2}. Figure 12 shows the thermal variation of the four single-ion levels for $L = 16.75$.

The influence of an applied field along z is shown in Figs. 13(a) and 13(b). H_z stabilizes the quadratic phase and may introduce a second phase transition at low temperature from the orthorhombic to the quadratic phase. Figures 14(a) and 14(b) show the influence of a field H_x. The transitions in P are suppressed since they are second order; the crystal is always orthorhombic.

We look now for the possibility of purely dipolar ordering in the parameter $M_x = g_{15}\langle S_{15}\rangle + g_{35}\langle S_{35}\rangle$:

$$\mathcal{H} = N\mathcal{H}_c - \sum_{i,j} J_{ij}S_i^xS_j^x\ , \tag{26}$$

with

$$S_x = g_{15}S_{15} + g_{35}S_{35}\ ,$$

$$\mathcal{H}_0/N = \mathcal{H}_c - H_{15}S_{15} - H_{35}S_{35}\ . \tag{27}$$

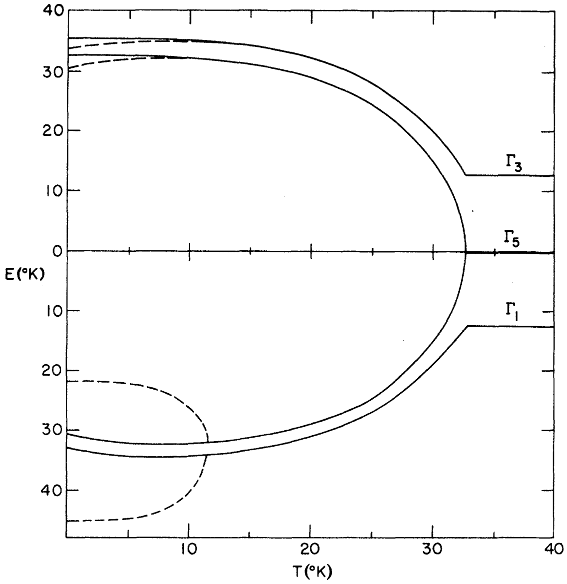

FIG. 12. Thermal variation of the energy levels of Tb^{3+} in $TbVO_4$ (in dashed lines for the case of a possible dipolar transition).

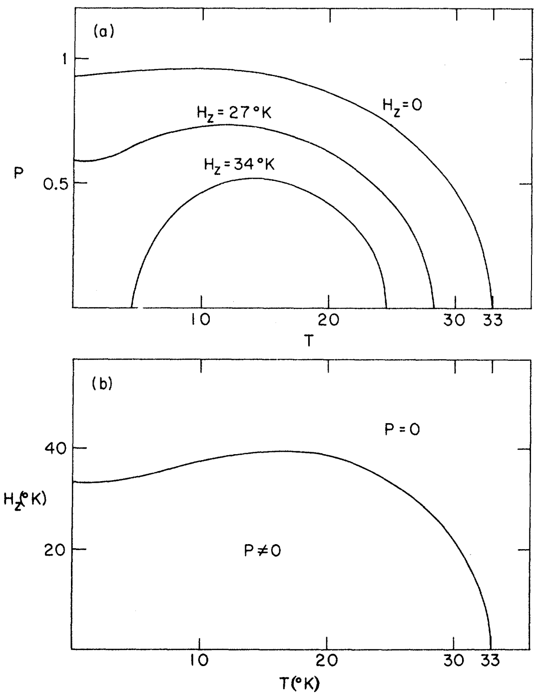

FIG. 13. (a) Influence of a field H_z on the thermal variation of P in TbVO$_4$. (b) Phase diagram in the (T, H_z) plane.

We have now

$$Z_0\langle S_{15}\rangle = \frac{1}{\beta}\frac{\partial Z_0}{\partial H_{15}} , \qquad (28a)$$

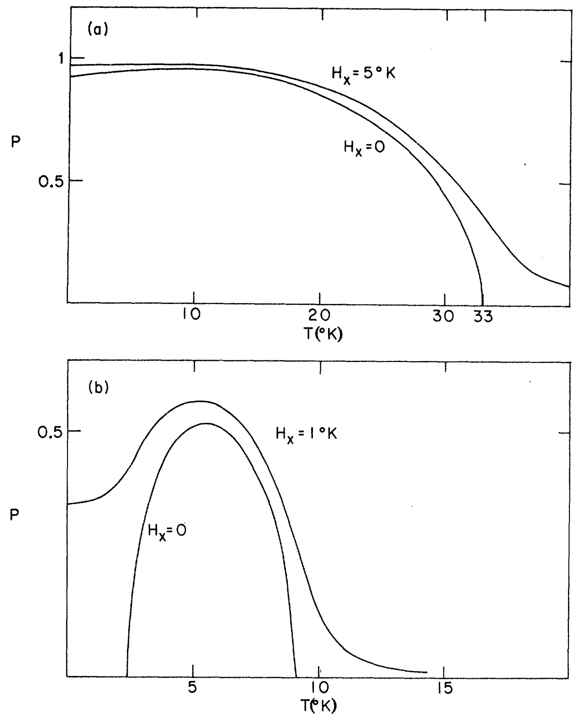

FIG. 14. Influence of a field H_x on the thermal variation of P in TbVO$_4$; (a) for $L = 16.75$ °K; (b) for $L = 8$ °K.

$$Z_0\langle S_{35}\rangle = \frac{1}{\beta}\frac{\partial Z_0}{\partial H_{35}} , \qquad (28b)$$

$$\phi_0 = -(1/\beta)\ln Z_0 + H_{15}\langle S_{15}\rangle + H_{35}\langle S_{35}\rangle$$

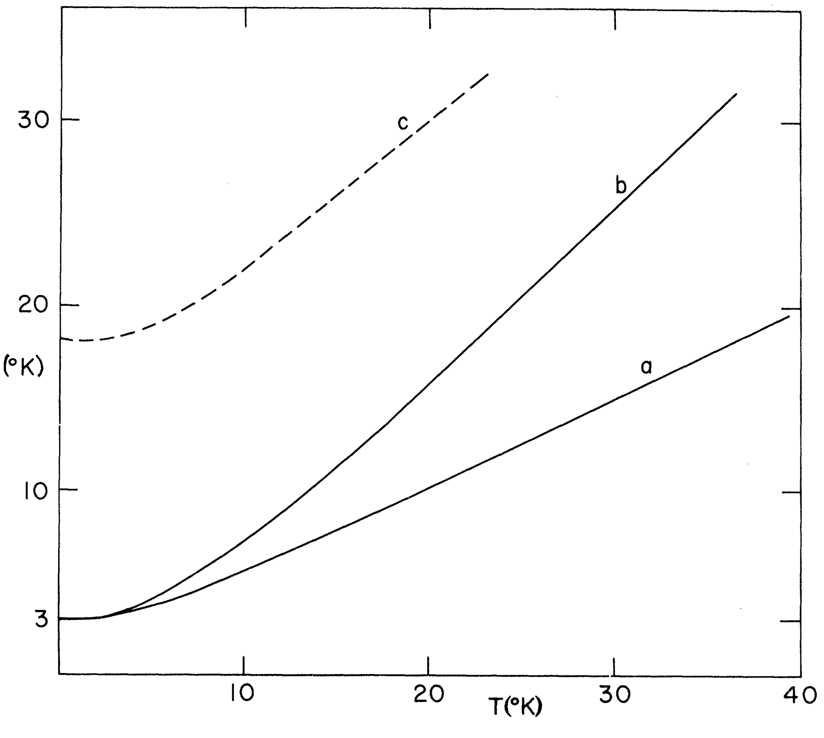

FIG. 15. Phase diagram in the (T, J) plane for the dipolar transition in TbVO$_4$; (a) $g_{15} = g_{35}$; (b) $g_{35} = 0$; (c) $g_{15} = 0$ (the transition is then first order).

$$-J(g_{15}\langle S_{15}\rangle + g_{35}\langle S_{35}\rangle)^2 \ . \quad (29)$$

The conditions $\partial\phi_0/\partial H_{15} = \partial\phi_0/\partial H_{35} = 0$ give $H_{15} = 2g_{15}JM$ and $H_{35} = 2g_{35}JM$. Suppose that $g_{15} = g_{35}$ and $\Delta_1 = \Delta_3 = \Delta$. The eigenvalues of $\mathcal{H}_0$ are 0, 0, $\pm\lambda$, with $\lambda^2 = \Delta^2 + 2H_{13}^2$:

$$Z_0 = 2(1+\cosh\beta\lambda) \ , \quad (30)$$

$$M_x = \frac{4JM_x}{\lambda}\ \frac{\sinh\beta\lambda}{1+\cosh\beta\lambda} \ , \quad (31)$$

with

$$\lambda^2 = \Delta^2 + 8J^2M_x^2 \ . \quad (32)$$

The temperature of the possibly second-order phase transition in M_x is given by

$$4J(\sinh\beta\Delta)/\Delta = 1 + \cosh\beta\Delta \quad (33)$$

and for $\beta\Delta \ll 1$, $kT_{M_x} \simeq 2J$.

If $g_{15} = g_{35}$, as well as if $g_{15} \neq 0$ and $g_{35} = 0$, the transition is in fact second order, and there is a threshold value of J (Fig. 15). If $g_{15} = 0$ and $g_{35} \neq 0$ the threshold value of J is much higher and the transition is first order.

We study now the possibility of successive dipolar and quadrupolar ordering in $TbVO_4$, although no dipolar transition has been yet reported below 1 °K. The Hamiltonian is then

$$\mathcal{H} = N\mathcal{H}_c - \sum_{i,j} L_{ij}P_iP_j - \sum_{i,j} J_{ij}S_i^xS_j^x \ .$$

If J is large enough, the quadrupolar transition is followed by a dipolar transition (Fig. 12, dashed lines). Figures 16(a) and 16(b) show the phase diagram in the (T, J) plane for values of L such that there is one or two quadrupolar transitions; for $L = 8$ °K, one, two, or three successive transitions are possible.

VI. CONCLUSION

We have given a molecular-field treatment of the dipolar and quadrupolar phase transitions observed in rare-earth vanadates. Pytte and Stevens have provided a physical explanation for these transitions, based on the semiclassical theory of crystalline field.[17] We note that our description of the phase transitions is correct only when the whole crystal field band[17] (determined by the classical minima of the crystalline potential) is considered. This was the case for $TbVO_4$, $DyVO_4$, and $TmVO_4$, but not for $TbPO_4$ where the minima are neither along the c axis nor in the a-b plane. As noted in Sec. II, the consideration of only the ground crystalline level Γ_5 describes dipolar ordering along the c-axis or quadrupolar ordering in the a-b plane. However, in $TbPO_4$, the moments are oriented 40° off the c axis, and a distortion follows dipolar ordering. Similarly, in $DyAsO_4$,[18] the moments are oriented 22° off the a or b axis, in the a-b plane, below T_N. Inclusion of excited crystalline levels should remove the difficulty by introducing anisotropy in the [110] or [001] plane. Inclusion of excited levels in the case of $TbVO_4$ and $DyVO_4$ would on the contrary bring no new feature to the description of the phase transitions.

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APPENDIX

Because of the complexity of the crystal field band $(\Gamma_1 + \Gamma_5 + \Gamma_3)$ of Tb^{3+}, it is not possible to describe it by using an effective spin $\frac{3}{2}$. As suggested by Pytte and Stevens,[6] we may use two effective spins $\frac{1}{2}$, $\vec{\sigma}$ and $\vec{\tau}$, and express the dipolar and quadrupolar operators as functions of the components of $\vec{\sigma}$ and $\vec{\tau}$ (a similar method has been used to describe the system singlet-triplet).[10] However, the form chosen in Ref. 6 to represent the crys-

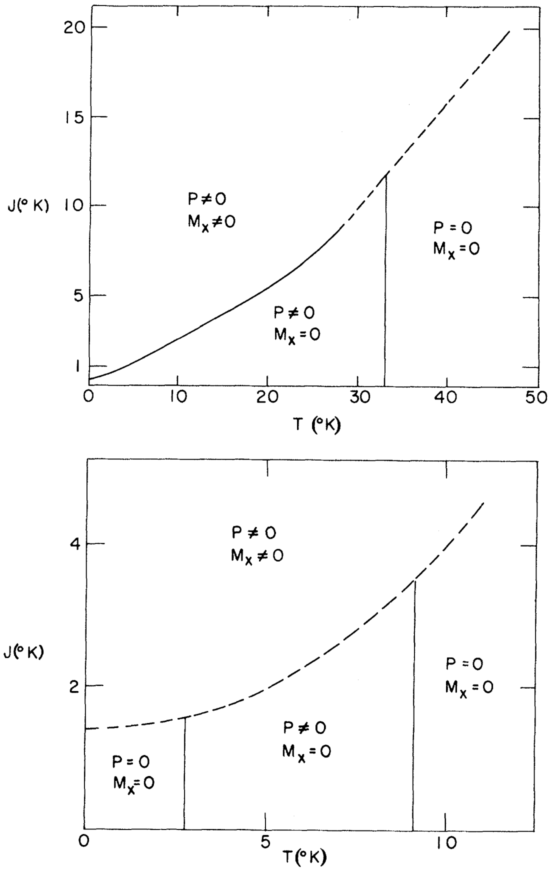

FIG. 16. Dipolar and quadrupolar ordering in $TbVO_4$; phase diagram in the (T, J) plane; (a) for $L = 16.75$ °K; (b) for $L = 8$ °K. First-order transitions are represented by dashed lines.

talline field energy $\mathcal{H}_c$ is not symmetrical in $\vec{\sigma}$ and $\vec{\tau}$ and we shall choose a slightly different one:

$$\mathcal{H}_c = \Delta(1+\delta\sigma^z)(1+\delta'\tau^z)+\Delta' .$$

We want the levels $|\tfrac{1}{2}-\tfrac{1}{2}\rangle = |+-\rangle$ and $|-\tfrac{1}{2}\tfrac{1}{2}\rangle = |-+\rangle$ to have the same energy, whence $\delta=\delta'$, and we take this energy as an origin, whence $\Delta' = -\Delta(1-\tfrac{1}{4}\delta^2)$. Δ and δ are now found easily as functions of the separations Δ_1 and Δ_3 between the doublet Γ_5 and each singlet $\Gamma_1(|++\rangle)$ or $\Gamma_3(|--\rangle)$:

$$\delta = 2(\Delta_3-\Delta_1)/(\Delta_3+\Delta_1)$$

and

$$\Delta = (\Delta_3+\Delta_1)^2/4(\Delta_3-\Delta_1) .$$

$|+-\rangle$ and $|-+\rangle$ being the basis of the doublet Γ_5, S^z is diagonal if $S^z = g_5(\sigma^z-\tau^z)$. But S^x is represented by $g(\sigma^x-\tau^x)$ only if $g_{35}=g_{15}=g$, and in this case $S^y = g(\sigma^y-\tau^y)$. If $g_{35}\neq g_{15}$, the expression of S^x is more complicated. As suggested by the expression of $\mathcal{H}_c$, the axial operator Q may be represented by

$$Q = Q_1(1+q\sigma^z)(1+q\tau^z)+Q_2 ,$$

with

$$q = 2(q_1+q_3-2q_5)/(q_1-q_3) ,$$

$$Q_1 = (q_1-q_3)/2q, \quad Q_2 = Q_0 - Q_1 .$$

Finally, we have

$$P = p_x\sigma^x\tau^x + p_y\sigma^y\tau^y ,$$

with

$$p_x = 2(p_{13}+p_{55}), \qquad p_y = 2(p_{13}-p_{55})$$

and

$$P_{13} = 2(\sigma^x\tau^x - \sigma^y\tau^y) ,$$

$$P_{55} = 2(\sigma^x\tau^x + \sigma^y\tau^y) .$$

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