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Tunneling Model of Phase Changes in Tetragonal Rare-Earth Crystals

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The crystal-field theory for a rare-earth ion in tetragonal symmetry is studied in a semiclassical description. The low-lying quantum states are interpreted as tunneling states between classical minima. At low temperatures, spontaneous lattice distortions occur to lower some of the minima relative to others. The model is applied to $DyVO_4$ and $TbVO_4$ and is shown to lead to a good understanding of why they show phase changes and unusual paramagnetic properties.

Recently, it has been reported that the tetragonal rare-earth crystals $DyVO_4$ [1-5] and $TbVO_4$ [5,6] undergo changes in crystal structure[7] at low temperature due to spontaneous Jahn-Teller distortions resulting from the nearly degenerate quartet crystal-field ground states of Dy^{3+} and Tb^{3+}. The distortion in $DyVO_4$ corresponds to an $e_{xx}-e_{yy}$ strain, while in $TbVO_4$ the distortion e_{xy} is rotated by $\frac{1}{4}\pi$ about Oz. These distortions are closely connected with the magnetic properties. The materials become Ising-like in the distorted structure. Our purpose in this Letter is to show that an understanding of the observations can be obtained from an interpretation of crystal-field theory in terms of quantum-mechanical tunneling, and to note the consequences which then result.

The crystal field at a rare-earth ion can be taken as

$$V \equiv A_2^0\langle r^2\rangle\langle J\|\alpha\|J\rangle O_2^0 + \langle J\|\beta\|J\rangle\langle r^4\rangle(A_4^0 O_4^0 + A_4^4 O_4^4) + \langle J\|\gamma\|J\rangle\langle r^6\rangle(A_6^0 O_6^0 + A_6^4 O_6^4), \quad (1)$$

where O_n^m are equivalent operators and $\langle J\|\alpha\|J\rangle$, $\langle J\|\beta\|J\rangle$, and $\langle J\|\gamma\|J\rangle$ are tabulated parameters.[8] It will be particularly important that the signs of $\langle J\|\alpha\|J\rangle$, etc., alter as one moves from one rare-earth ion to another. The A_n^m are determined by the environment of the ion, and $A_n^m\langle r^n\rangle$ changes relatively little from one ion to the next. Inspection of the experimentally determined crystal-field-split energy levels in $DyVO_4$ and $TbVO_4$ show four closely spaced low-lying levels with a large separation from the next levels. To understand why this arrangement occurs we convert the equivalent operator into a "classical" crystal-field energy[9,10] by setting $J_x = J\sin\theta\cos\varphi$, $J_y = J\sin\theta\sin\varphi$, and $J_z = J\cos\theta$, neglecting the difference between $J(J+1)$ and J^2, and assuming the fourth-order term, $A_4^4\langle r^4\rangle\langle J\|\beta\|J\rangle J^4\sin^4\theta\cos 4\varphi$, to be dominant. Then V has four equal minima in the plane $\theta = \frac{1}{2}\pi$ at $\varphi = 0$, $\frac{1}{2}\pi$, π, and $\frac{3}{2}\pi$ for negative $\langle J\|\beta\|J\rangle$, and at $\varphi = \frac{1}{4}\pi$, $\frac{3}{4}\pi$, $\frac{5}{4}\pi$, and $\frac{7}{4}\pi$ for positive $\langle J\|\beta\|J\rangle$. (The sign of A_4^4 has been taken as positive.) At low temperatures the classical moment will lie in one of these minima. This cannot be the correct quantum-mechanical description because of tunneling, which suggests that appropriate tunneling linear combinations be used. Dy^{3+} $4f^9\,{}^6H_{15/2}$ has negative $\langle J\|\beta\|J\rangle$. For $DyVO_4$ we therefore postulate that the low-lying crystal-field states will approximate to

$$[N(\omega)]^{-1/2}\left(|J_x = \tfrac{15}{2}\rangle + \omega|J_y = \tfrac{15}{2}\rangle + \omega^2|J_x = -\tfrac{15}{2}\rangle + \omega^3|J_y = \tfrac{15}{2}\rangle\right), \quad (2)$$

where

$$|J_y = \tfrac{15}{2}\rangle = \exp(\tfrac{1}{2}i\pi J_z)|J_x = \tfrac{15}{2}\rangle,$$

etc., and where ω ranges over the four solutions of $x^4 = -1$. For Tb^{3+} $4f^8\,{}^7F_6$, the signs of both $\langle J\|\beta\|J\rangle$

and $\langle J\|\gamma\|J\rangle$ are reversed and the minima are rotated by $\frac{1}{4}\pi$ about Oz from the Dy^{3+} minima. We take

$$[N(\omega)]^{-1/2}[|J_X=6\rangle+\omega|J_Y=6\rangle+\omega^2|J_X=-6\rangle+\omega^3|J_Y=-6\rangle], \tag{3}$$

where ω satisfies $\omega^4=+1$ and OX and OY are rotated by $\frac{1}{4}\pi$ from Ox and Oy. For Tb^{3+} the expectation values of a tetragonal crystal field taken over the tunneling states of Eq. (3) give a singlet, doublet, singlet pattern with nearly equal spacings. This agrees with the observed pattern[5,6] and has identical symmetry properties. For Dy^{3+}, which is a Kramers ion, the tunneling states give a pair of doublets of the correct symmetry. Furthermore, in $DyVO_4$ a detailed crystal-field analysis has been undertaken by Cooke *et al.*[11] The overlaps of the crystal-field states with the tunneling states are all close to 1.

We next consider what happens as the temperature is lowered so that the higher tunneling states become depopulated. It may then become energetically favorable for the crystal to distort, to lower some of the minima relative to the others, even though work has to be done against the elastic forces in the lattice. The ion then no longer tunnels equally between all the minima, but is more often in some (the lower-energy ones) than others. It is particularly interesting that the type of distortion which is most effective is determined by the high-symmetry crystal field, for it is only those distortions which alter the minima which are effective. The relevant lattice–angular-momentum interactions for the two families $\varphi=0,\frac{1}{2}\pi,\pi,\frac{3}{2}\pi$ and $\varphi=\frac{1}{4}\pi,\frac{3}{4}\pi,\frac{5}{4}\pi,\frac{7}{4}$ contain, in the lowest power in $\vec{J}$, $G_1e(B_{1g})(J_x^2-J_y^2)$ and $2G_2e(B_{2g})J_xJ_y$, respectively, where B_{1g} and B_{2g} denote the symmetry of the deformation. In the classical approximation these may be written as

$$\begin{aligned} &G_1e(B_{1g})J^2\sin^2\theta\cos2\varphi,\\ &G_2e(B_{2g})J^2\sin^2\theta\sin2\varphi. \end{aligned} \tag{4}$$

Such terms split the four minima into two pairs for each of the two families, respectively, the members of each pair being separated by $\Delta\varphi=\pi$. This accounts for the different types of distortion in $DyVO_4$ and $TbVO_4$. No further splitting of a pair can occur, because the crystal field is of even parity. For one sign of distortion, one pair is lower; for the other sign, the other pair is lower. If one lowers the temperature from above that at which the distortion sets in, there is no way of knowing which particular pair will be favored. An applied magnetic field can select one of the four minima, the direction of $H_\perp$ determining the sign of the strain distortion. Changing the direction of $H_\perp$ by $\frac{1}{2}\pi$ interchanges the a and b axes. Magnetic switching of this kind has been observed both in $DyVO_4$[1,2] and $TbVO_4$.[6]

For a general tetragonal field, besides the cases discussed above there may be eight equal absolute minima at $\theta=\alpha,\pi-\alpha$, $\varphi=\beta,\beta+\frac{1}{2}\pi,\beta+\pi,\beta+\frac{3}{2}\pi$; or two absolute minima at $\theta=0,\pi$, depending on the magnitudes of the crystal-field parameters and on the signs of $\langle J\|\beta\|J\rangle$, etc. $DyPO_4$ may be an example of two minima at $\theta=0,\pi$. It does not undergo a transition, and each ion has a large moment along the z axis.[12] For the case with eight minima away from $\theta=\frac{1}{2}\pi$, two distortions are likely, one to separate them into two families of four, followed by another to split the low-lying four into two pairs. Phase transitions of this type have not been reported.

The nature of the phase change can be studied for the case of the four minima in the plane by describing the four tunneling states in terms of two sets of Pauli operators, σ and τ. For a non-Kramers ion the energy-level pattern is given by

$$(a+b\tau_3)(1+\sigma_3),\ \text{with } a=\tfrac{1}{4}(\Delta_1-\Delta_2),\quad b=\tfrac{1}{4}(\Delta_1+\Delta_2), \tag{5a}$$

and for a Kramers ion by

$$\Delta\sigma_3, \tag{5b}$$

where Δ, Δ_1, and Δ_2 are the temperature-independent constants defined in Fig. 1. The coupling to the lattice is of the form

$$ge\sigma_1, \tag{6a}$$

and

$$g_1e(1-\sigma_3)\tau_1+g_2e(1+\sigma_3)\tau_1 \tag{6b}$$

for Kramers and non-Kramers ions, respectively, where the deformations have B_{1g} symmetry for minima at $\varphi\equiv0 \bmod\frac{1}{2}\pi$, and B_{2g} symmetry for minima at $\varphi\equiv\frac{1}{4} \bmod\frac{1}{2}\pi$. To give a brief description of the phase transition we assume for simplicity that the spin interacts only with a single normal mode of the lattice. For Kramers ions with $\varphi=0$ ($DyVO_4$) the free energy in a mean-field approximation is then given by

$$F=\tfrac{1}{2}C\langle e\rangle^2-nkT\ln(2\cosh\beta\lambda). \tag{7}$$

Here n is the number of rare-earth ions per unit

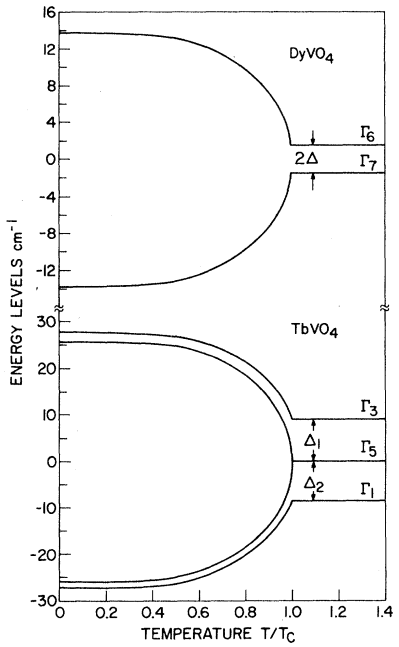

FIG. 1. Calculated level structure of $DyVO_4$ and $TbVO_4$. For $TbVO_4$ the splitting of the level doubly degenerate for $T > T_c$ is proportional to the distortion.

cell, $\lambda = (\Delta^2 + g^2\langle e\rangle^2)^{1/2}$ is the mean field, and C is the force constant for the normal mode considered. The thermal average $\langle e\rangle$ measures the distortion and is determined by minimizing the free energy. It satisfies

$$C\langle e\rangle = g^2 n\langle e\rangle \lambda^{-1}\tanh\beta\lambda. \tag{8}$$

At high temperatures the minimum free energy occurs with zero distortion, but at a critical temperature T_c defined by

$$\frac{1}{\Delta}\tanh\beta_c\Delta = \frac{C}{ng^2} = \frac{1}{\lambda(T=0)}, \tag{9}$$

the distortion ceases to be zero and increases with decreasing temperature. Accompanying the distortion there is a change in the energy-level pattern. The temperature dependence of the two low-lying Kramers doublets in the mean-field approximation is shown[13] in Fig. 1 for $\Delta = 1.5$ cm^{-1} and $ng^2/C = 13.8$ cm^{-1}.[5]

When only coupling to elastic strain is included, the mean field level separation is equal to the frequency of a $q = 0$ collective excitation, $\omega(q=0) = \pm 2\lambda$. For $q \neq 0$, the modes are dispersive as a result of the coupling with acoustic phonons. The elastic constant $C_{11} - C_{22}$, associated with the distortion $e_{xx} - e_{yy}$, vanishes at the transition point. The elastic constants may be calculated in the usual way as the second variation of the free energy, in the presence of a uniform deformation, with respect to this deformation. For $C_{11} - C_{12}$ we obtain

$$\begin{aligned} C_{11} - C_{12} &= 2ng^4\langle e\rangle^2\lambda^{-3}(\tanh\beta\lambda - \beta\lambda\,\mathrm{sech}^2\beta\lambda), \quad T < T_c, \\ &= 2ng^2\Delta^{-1}(\tanh\beta_c\Delta - \tanh\beta\Delta), \quad T > T_c. \end{aligned} \tag{10}$$

If, instead, interaction with an internal strain is considered, the frequency of a coupled pseudospin–optical-phonon mode vanishes at the transition point with the level splitting 2Δ of the uncoupled system recovered only in the limit $T \to \infty$. When calculated from linearized equations of motion describing fluctuations about the mean-field values, the collective normal-mode frequencies are given by

$$(\omega^2 - 4\lambda^2)[\omega^2 - \omega_0^2(q)] = 4g^2 n(\Delta/\lambda^2)\tanh\beta\lambda,$$

where $\omega_0(q)$ is the frequency of the optical phonon. Because these modes couple to the elastic strain, anomalies in the elastic constants are obtained also when the coupling to an internal strain is predominant.

In the distorted structure the lowest Kramers doublet is

$$|A\rangle = \alpha_+|3\rangle + \alpha_-|-1\rangle, \quad |A'\rangle = \alpha_+|-3\rangle + \alpha_-|1\rangle,$$

where

$$\alpha_\pm = \tfrac{1}{2}\sqrt{2}\,[1 \pm \Delta/\lambda(T)]^{1/2}$$

and the states $|n\rangle$ have $\omega = \exp(in\pi/4)$ in Eq. (2). At $T = 4.5°K$ with these states, $\Delta = 1.5$ cm^{-1} and $\lambda = 13.8$ cm^{-1}, the principal g values are $g_a = 20.0$, $g_b = 0$, and $g_c = g_z = 0.017$, in close agreement with the measured low-temperature values.[2,3] The g values for the lowest doublet for $T > T_c$ ($\alpha_+ = 1$, $\alpha_- = 0$) are $g_a = g_b = g_\perp = 9.9$ and $g_c = g_\parallel = 0.16$. For the other doublet the g values are $g_\perp = 10.1$ and $g_\parallel = 0.15$. The observed splittings[5] of doubly degenerate optical-phonon frequencies may be accounted for by interactions of the form $ge(B_{1g})Q_1Q_2$ and $g'\sigma_1 Q_1 Q_2$, where Q_1 and Q_2 denote the optical-phonon normal-mode coordinates.

For non-Kramers ions with minima at $\varphi \equiv \frac{1}{4}\pi$

mod$\frac{1}{2}\pi$ ($TbVO_4$), the free energy may be written

$$F = \tfrac{1}{2}C\langle e_{12}\rangle^2 - nkT\ln(2\cosh\beta\lambda + e^{-\beta\lambda_3} + e^{-\beta\lambda_4}),$$

where 2λ describes the splitting of the level which is degenerate for $T > T_c$,

$$\lambda_{1,2} = \pm\lambda = \pm 2g_1\langle e\rangle,$$

while $\lambda_{3,4}$ denote the position of the singlet levels,

$$\lambda_{3,4} = 2a \pm (4b^2 + 4g_2{}^2\langle e\rangle^2)^{1/2}.$$

For the states given by Eq. (3), $g_1/g_2 = (31\times 33)^{1/2}/32$ and $\Delta_1/\Delta_2 = 33/31$. The calculated mean-field energy-level pattern for $TbVO_4$ is shown in Fig. 1 for $\Delta_2 = 8.5\ cm^{-1}$ and $g\langle e\rangle = 12.4\ cm^{-1}$ at 16°K.[5,6]

For some choices of parameters, the four-level model used to describe $TbVO_4$ does not give a phase transition. For still other values the lattice is distorted only for an intermediate temperature range, returning to tetragonal symmetry at low temperatures.

Structural transitions have also been observed in cubic[14] and trigonal[15] rare-earth compounds. If the fourth-order term is assumed to be dominant, one obtains for the cubic crystal field either six minima in the $\langle 100\rangle$ directions or eight minima in the $\langle 111\rangle$ directions,[9] depending on the sign of $\langle J\|\beta\|J\rangle$. Tetragonal and trigonal distortions are favored, respectively, for these two cases. Experimentally, tetragonal distortions are observed for Nb^{3+}, Dy^{3+}, and Ho^{3+} compounds[14] for which $\langle J\|\beta\|J\rangle$ is negative, and trigonal distortions for Tb^{3+} compounds[14] for which $\langle J\|\beta\|J\rangle$ is positive. The lowering of the symmetry changes the magnetic interactions and this may explain the nearly simultaneous magnetic ordering in many of these compounds. The structural transitions in the cubic rare-earth compounds have also been described as due to quadrupole-quadrupole interactions.[16]

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