

Symmetry in order-disorder changes of molecular clusters

Ana Proykova,¹ Dessislava Nikolova,¹ and R. Stephen Berry²

¹*Faculty of Physics, University of Sofia, 5 James Bourchier Blvd., Sofia-1126, Bulgaria*

²*Department of Chemistry, the University of Chicago, Chicago, Illinois 60637*

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Clusters of octahedral AF_6 molecules transform when cooled from a body-centered-cubic, orientationally disordered phase to a monoclinic, orientationally ordered phase in a two-step process. Recently, the higher-temperature transition has been shown to be a finite-system counterpart of a first-order transition. Here, with the help of symmetry-adapted rotator functions, we show that the lower-temperature transition is continuous. With our analytical model, we predict a temperature of 27 K for this transition, for a 59-molecule cluster of TeF_6 , consistent with the ~ 30 -K result from canonical Monte Carlo calculations.

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I. INTRODUCTION

Free clusters of ~ 100 or more octahedral molecules of SF_6 (Refs. 1 and 2) and TeF_6 (Ref. 3) solidify in body-centered-cubic (bcc) structures with molecules disordered orientationally. A further decrease of temperature produces a phase transition to a more orientationally ordered phase with a lattice structure of a lower, monoclinic symmetry, as diffraction experiments have shown.⁴⁻⁷ Numerical experiments show analogous structural transformations.⁸⁻¹² Our previous molecular-dynamics simulations^{12,13} indicated two steps in the ordering structural transition. First, when the solid cluster is cooled from near freezing, it undergoes a transition from a bcc orientationally disordered phase to a partially ordered monoclinic phase. The two phases coexist dynamically,^{14,15} indicative of the small-system counterpart of a first-order phase transition. A second transition, monoclinic to monoclinic but from partially ordered to completely ordered orientations, occurs with a further temperature decrease.

There has been no clear indication of the nature of this second transition: the absence of coexisting phases is a necessary but not sufficient condition to claim that this is a continuous transition. In fact, it might be a weak first-order transition, distorted by the presence of a symmetry-breaking surface.

In order to understand the two-step solid-solid transformation induced by temperature changes, we develop a microscopic, symmetry-based description of the ordering of the molecular centers of mass and then of the axes of symmetry, in terms of point group theory.¹⁶ Such a description makes it possible to calculate the relative contributions of various interactions to the total potential of the cluster, and thereby to infer the dominant mechanism responsible for a specific transition. The methodology was developed¹⁷ to describe the rotation-rotation interactions in C_{60} and translation-rotation in KCN.¹⁸ A broader aim is to determine the nature and origins of the temperature-driven solid-solid transformations of clusters of rigid molecules (intramolecular vibrations are neglected), and to gain insights into the nature of second-order and weak first-order transitions.

Solid (structural) changes in a cluster take place when some distortion develops in active constituent groups, either individually or collectively. The distortion is typically characterized by a change in the lattice symmetry. A change in a

suitable order parameter¹⁹ describes the relaxation of the system in terms of its broken symmetry. The Landau theory gives a qualitative description of continuous phase transitions if the order parameter is a scalar and the so-called marginal spatial dimension is exceeded.²⁰ Being a mean-field theory, it does not allow a detailed description of the various interactions and their relative contribution to the total potential at different temperatures. It is instructive to implement a microscopic description to elucidate the phase changes in small systems, and then to connect them to Landau theory for the corresponding bulk matter.

Here, we adopt a specific model¹⁷ to describe the dynamic orientational disorder of the high-temperature phase, and the transition to the orientationally ordered monoclinic structure of clusters of octahedral molecules. The model is applicable to any cluster composed of 59 molecules or more. This number of molecules ensures that at least one primitive cell for the high- T structure (bcc) is in a proper surrounding demanded by the group symmetry operations for a lattice.

Solid-solid transitions of free nanoclusters tend to initiate on the surface.^{9,13,21} The current analysis assumes that in the vicinity of phase transitions molecules change their immediate neighborhood from disordered to more ordered structures when the temperature decreases. With a decrease of the kinetic energy, the orientational dependence of the interacting potential becomes relatively more and more pronounced. Hence, with cooling, there is a relative increase in the angle-dependent interactions that lead to a lower-temperature phase change.

In Secs. II and III we consider only the lattice symmetry of the volume, with the (interior) molecules treated as having all the neighbors required by the corresponding point group of a crystal. Surface effects are included in Sec. IV in the application example by explicit calculation of binding energies: the surface molecules have larger amplitudes of motion around the lattice points, and are of course less strongly bound than those in the interior. Another alternative to treating the surface explicitly would be to use continuous symmetry measures^{22,23} or a perturbation approach such as “near symmetry groups.”²⁴

The model for the orientation order-disorder transformation of molecules in a given surrounding symmetry is described in Sec. II. We use rotator functions²⁵ to compute the

various contributions to the interaction potential described in Sec. III, and apply the microscopic model to predict the transition temperature of a cluster in Sec. IV. The computed temperature from the analytical theory is in good agreement with the computer experiments performed with Monte Carlo and molecular-dynamics methods. The theory presented here reveals the origin of the two-step order-disorder phase transition in molecular clusters, and shows that clusters as small as 59-molecule aggregates of octahedral molecules have properties which can be correlated with these of the bulk material.

II. A SINGLE MOLECULE AT A SPECIFIC MOLECULAR SITE

In order to take into account the symmetries of the AF_6 molecule and of the molecular site in the cluster we use concepts from the theory of orientationally disordered substances.^{26,16} We consider that the AF_6 molecules with O_h symmetry are rigid, and are located either in an O_h local environment at elevated temperatures or in a C_{2h} local environment below the transition temperature. The location of each molecule is specified by its center of mass. Orientation disorder characterizes the high-temperature phase.

We refer to (i) a space (laboratory) axis system XYZ fixed at the cluster's center of mass, (ii) a nonrotating system $X'Y'Z'$ parallel to XYZ but with its origin translating with the molecular center of mass, and (iii) a rotating, body-fixed system xyz . For rigid molecules, these axes coincide with the principal axes of inertia.

At the first stage, we consider molecular translation and rotation separately. Molecular translation is described as the motion of the molecular centers of mass in the XYZ coordinates. The xyz orientation in the XYZ system is specified by the three Euler angles $\omega = (\alpha, \beta, \gamma)$, where α ($0 \leq \alpha \leq 2\Pi$) and β ($0 \leq \beta \leq \Pi$) are the ordinary polar coordinates of the z axis in the XYZ system, and γ ($0 \leq \gamma \leq 2\Pi$) is an angle in the xy plane measuring the clockwise rotation about the z axis.

We describe molecular sites and molecular orientation in orientationally disordered high- T crystals in terms of symmetry-adapted rotator functions¹⁶ $S(\Omega)$, $\Omega = (\theta, \varphi)$, used by James and Keenan²⁷ to describe solid methane, having a tetrahedral symmetry. These angles, the conventional colatitude and azimuth, describe the orientation of a fixed vector in the molecule. For a tetrahedral (octahedral, as well) symmetry and a rigid molecule, one can choose one of the bonds as the fixed vector.

The orientational changes at a *cubic* site are expressed in terms of site-symmetry-adapted functions¹⁶

$$S_l^\tau(\Omega) = \sum_{m=-l}^l Y_l^m(\Omega) \alpha_l^{m\tau}, \quad (1)$$

where $\tau = (G, \Gamma, p, \rho)$ indicates the irreducible representations Γ of the group G , p distinguishes representations that occur more than once, and ρ denotes the rows of a given representation; $Y_l^m(\Omega)$ are the spherical harmonics; the coef-

ficients α_l^m are tabulated.¹⁶ The functions $S_l^\tau(\Omega)$ form a complete basis in Ω -space if all l 's are included in the sum [Eq. (1)].

A. Molecular axes aligned with the cluster's center of mass

Let an octahedral molecule have an initial orientation ω in which the molecular axes coincide with the laboratory system axes. The resulting orientational density distribution is expanded in terms of spherical harmonics $Y_l^m(\Omega)$ in the same way as in Eq. (1). The molecular symmetry requires that $l=0,4,6,\dots$, and only certain linear combinations of Y_l^m occur. For each allowed l , we determine the molecular symmetry-adapted functions $S_l^\lambda(\Omega)$, where λ refers to the identity representation of the cubic group O_h .¹⁶ The $l=4$ manifold of the symmetry-adapted functions reduces to A_{1g} , E_g , T_{1g} , and T_{2g} .

At low temperatures, clusters of AF_6 molecules adopt a monoclinic structure C_{2h} .³ The $l=4$ manifold of the symmetry-adapted functions reduces to the representations $5A_g$ and $4B_g$ under $G \equiv C_{2h}$. A_g is the representation which belongs to O_h and C_{2h} .

B. Arbitrary orientation of a molecule at its site

For a molecule in an arbitrary orientation, rotated at ω with respect to the orientation discussed in Sec. II A, the symmetry-adapted function becomes

$$\hat{R}(\omega) S_l^\lambda(\Omega^b) = \sum_{k=-l}^l \sum_{m=-l}^l Y_l^m(\Omega^s) D_l^{mk}(\omega) \alpha_l^{k\lambda}, \quad (2)$$

with $\hat{R}(\omega)$ the rotator operator and $D_l^{mk}(\omega)$ the Wigner matrices; Ω^b and Ω^s determine the polar angle in the molecular (body) and laboratory (space) systems, respectively. In Eq. (2) we put the spherical harmonics $Y_l^m(\Omega^s)$, determined from the inverse of equation (1),

$$\begin{aligned} \hat{R}(\omega) S_l^\lambda(\Omega^b) &= \sum_{\tau, m, k} S_l^\tau(\Omega^s) (\alpha_l^{m\tau}) D_l^{mk}(\omega) \alpha_l^{k\lambda} \\ &= \sum_{\tau} S_l^\tau(\Omega^s) \Delta_l^{\tau\lambda}(\omega), \end{aligned} \quad (3)$$

where

$$\Delta_l^{\tau\lambda}(\omega) = \sum_{k=-l}^l \sum_{m=-l}^l (\alpha_l^{m\tau}) D_l^{mk}(\omega) \alpha_l^{k\lambda} \quad (4)$$

are the rotator functions defined by the symmetry properties of the molecule $\alpha_l^{k\lambda}$ and of the site $\alpha_l^{m\tau}$. Equation (3) relates the symmetry-adapted functions $S_l^\lambda(\Omega^b)$ for the body (molecular) system to the symmetry-adapted functions $S_l^\tau(\Omega^s)$ for the system—a cluster with a specific symmetry.

The rotator function's average value $\bar{\Delta}_l^{\tau\lambda}(\omega)$ is zero in the disordered phase and nonzero in the orientationally ordered phase. This property makes it suitable to be chosen as an *order parameter* for the solid-solid transformations, as suggested by James and Keenan for solid CD_4 ($l=3$).²⁷

III. INTERMOLECULAR POTENTIAL EXPANSION IN TERMS OF ROTATOR FUNCTIONS

So far we have considered a single molecule at a specific site. The orientational configuration of N molecules in the cluster is given by $\Delta_l^{\tau\lambda}(\omega(n)) = \Delta_l^{\tau\lambda}(n)$ where $n = 1, 2, \dots, N$, labels each molecule's center at its site position \mathbf{r}_n . The total potential V is the sum over N molecules of interactions between two molecules n and n' , each of which can be written as a sum of atom-atom potentials¹⁰

$$V = \sum_{n < n'}^N \sum_{\nu, \nu'}^{N_a} V(n, \nu; n', \nu'), \quad (5)$$

where (n, ν) labels the ν th atom in the n th molecule at site \mathbf{r}_n , with N_a atoms. The atom-atom potential $V(n, \nu; n', \nu')$ depends on the distance $r_{\nu\nu'}$ between the atoms ν and ν' . The position of the ν th atom in the n th molecule with respect to the space system is given by

$$\mathbf{R}(n, d^\nu) = \mathbf{r}_n + \mathbf{r}_{n\nu} + \mathbf{u}(n),$$

with $\mathbf{u}(n)$ the displacement of the n th molecule from its equilibrium site position \mathbf{r}_n ; the vector $\mathbf{r}_{n\nu}[d^\nu, \Omega_\nu(n)]$ is determined by the length d^ν and the orientation $\Omega_\nu(n)$ in the space system. For a rigid molecule, d^ν is equal to the bond length.

In order to determine the translation-rotation coupling we need to expand the pair potential by considering a nonrigid lattice. Expansion of Eq. (5) in terms of the displacements $\mathbf{u}(n)$ yields a sum over terms of p th order,

$$V(n, n') = \sum_{p=0}^{\infty} \sum_{\nu, \nu'} \frac{1}{(p!)} V_{i_1 \dots i_p}^{(p)}(r_{\nu\nu'}) [u_{i_1}(n) - u_{i_1}(n')] \dots [u_{i_p}(n) - u_{i_p}(n')], \quad (6)$$

with the notation

$$\mathbf{r}_{n\nu\nu'} = |\mathbf{R}(n, d^\nu) - \mathbf{R}(n', d^{\nu'})| = |\mathbf{r}(n) - \mathbf{r}(n') + \mathbf{u}(n) - \mathbf{u}(n') + \mathbf{r}_{n\nu} - \mathbf{r}_{n'\nu'}|$$

$$V_{i_1 \dots i_p}^{(p)}(r_{\nu\nu'}) = \frac{\partial^p V(r_{\nu\nu'})}{\partial [\mathbf{u}(n) - \mathbf{u}(n')]_{i_1} \dots \partial [\mathbf{u}(n) - \mathbf{u}(n')]_{i_p}}. \quad (7)$$

The coefficients $V^{(p)}$ contain the orientational dependence of the molecules at the sites n and n' . We expand them in terms of S_l^τ [Eq. (1)]. In the following we write $S_\mu(\nu)$ for $S_l^\tau(\Omega_\nu)$, where $\mu \equiv \mu(\tau, l)$:

$$V_{i_1 \dots i_p}^{(p)}(r_{\nu\nu'}) = \sum_{\mu, \mu'} c_{i_1 \dots i_p \mu \mu'}^{(p)}(n, n') S_\mu(\nu) S_{\mu'}(\nu'). \quad (8)$$

The coefficients $c_{i_1 \dots i_p \mu \mu'}^{(p)}(n, n')$ are determined by integrating the pairwise potential over the possible orientations of $r_{n\nu}$ and $r_{n'\nu'}$:

$$c_{i_1 \dots i_p \mu \mu'}^{(p)}(n, n') = \int d\Omega_\nu \int d\Omega_{\nu'} V_{i_1 \dots i_p}^{(p)}(n, n') S_\mu(\nu) S_{\mu'}(\nu'). \quad (9)$$

Now we substitute $V^{(p)}$ from Eq. (8) into Eq. (6), and introduce the molecular form factor g_l^λ :

$$V(n, n') = \sum_p \sum_{\mu, \mu'} \frac{1}{p!} c_{i_1 \dots i_p \mu \mu'}^{(p)}(n, n') g_l^\lambda g_{l'}^\lambda \Delta_\mu(n) \Delta_{\mu'}(n') \times [u_{i_1}(n) - u_{i_1}(n')] \dots [u_{i_p}(n) - u_{i_p}(n')]. \quad (10)$$

The molecular form factor is defined for allowed l as $g_l^\lambda = \sum_{\nu=0}^{N_a} S_l^\lambda[\Omega_\nu(n)]$ if the molecular axes coincide with the space axes or as $\sum_\nu S_\mu(\nu) = g_l^\lambda \Delta_\mu(\omega)$ if the molecule is rotated at an angle ω . Molecular and site symmetry considerations restrict the number of terms in the sums in Eq. (10).

A. Rotation-rotation interaction

The value $p=0$ corresponds to a rigid lattice (no motions of the molecular centers of mass). This case yields only rotation-rotation interaction between molecules, with $\mu \neq (0,0)$ and $\mu' \neq (0,0)$:

$$V^{(0)}(n, n') = \sum_{\mu, \mu'} c_{\mu \mu'}^0(n, n') g_l^\lambda g_{l'}^\lambda \Delta_\mu(n) \Delta_{\mu'}(n'). \quad (11)$$

The total rotation interaction is the sum over all molecules, $V^{RR} = \sum_{n, n'}^N V^{(0)}(n, n')$.

The matrix of rotation-rotation interactions is defined by

$$\hat{J}_{\mu \mu'}(n, n') = c_{\mu \mu'}^{(0)}(n, n') g_l^\lambda g_{l'}^\lambda, \quad (12)$$

where the interaction matrices $c_{\mu \mu'}^{(0)}(n, n')$ follow from Eq. (9). Their structure depends on the symmetry of S_μ and on the relative position (n, n') of two interacting molecules on a lattice with symmetry specified by τ .

To calculate the transition temperature we need the total field V^R acting on the molecule at site $\mathbf{r}(n)$. The zeroth approximation treats spherically symmetric molecules $\mu' = (0,0)$ acting on a molecule n with $\mu \neq (0,0)$ on a rigid lattice $p=0$:

$$V^{(0)}(n, n')|_{l'=0} = \sum_{\mu} c_{\mu}^{(0)}(n, n') g_l^\lambda g_0^\lambda \Delta_\mu(n).$$

Setting $\mu' = (0,0)$ yields

$$S_{\mu'} = S_0^{A1g} = (4\pi)^{-1/2} \quad \text{and} \quad g_0 = N_a (4\pi)^{-1/2}.$$

The coefficients $c_{\mu}^{(0)}(n, n')$ become

$$c_{\mu}^{(0)}(n, n') = \frac{1}{\sqrt{(4\pi)}} \int d\Omega_\nu \int d\Omega_{\nu'} V^{(0)}(n, n') S_\mu(\nu).$$

Let us denote the interaction matrices $c_{\mu}^{(0)}(n, n')$ weighted with the molecular factors g_l^λ and g_0^λ by v_a^R , where a is an index for (l, A_{1g}, p, ρ) :

$$v_a^R = \sum_{n'} c_a^{(0)}(n, n') g_l^\lambda g_0^\lambda. \quad (13)$$

The crystal field acting on the molecule n is

$$V^R(n) = \sum_a v_a^R \Delta_a(n). \quad (14)$$

The rotator functions $\Delta_l^{A_{1g}}(n)$ in Eq. (14) are cubic functions.

B. Translation-rotation and translation-translation interaction

The pair translation-rotation interaction follows from Eq. (10) for $p=1$, $\mu \neq (0,0)$, and $\mu' = (0,0)$:

$$V^{TR}(n, n') = V^{(1)}(n, n') = \sum_{i\mu} c_{i\mu}^{(1)}(n, n') g_l^\lambda g_0^\lambda \Delta_\mu(n) \times [u_i(n) - u_i(n')]. \quad (15)$$

The sum over all molecules yields the total bilinear interaction $V^{TR} = \sum_{n, n'} V^{TR}(n, n')$. The translation-rotation interaction is caused by the change of the orientational potential due to the displacement of nearest neighbors.

The pair translation-translation interaction is obtained from Eq. (10) for $p=2$, $\mu' = (0,0)$, and $\mu = (0,0)$:

$$V^{TT}(n, n') = V^{(2)}(n, n') = \sum_{i_1, i_2} \frac{1}{2} c_{i_1 i_2}^{(2)}(n, n') g_0^\lambda g_0^\lambda \times [u_{i_1}(n) - u_{i_1}(n')] [u_{i_2}(n) - u_{i_2}(n')]. \quad (16)$$

This gives a total translation-translation interaction $V^{TT} = \sum_{n, n'} V^{TT}(n, n')$. Now the total potential separates:

$$V = V^R + V^{TT} + V^{TR} + V^{RR}. \quad (17)$$

Equation (17) may be expanded with higher order terms, which might become important in some structural phase transitions.²⁸

IV. APPLICATION OF THE ROTATOR FUNCTIONS TO STRUCTURAL TRANSITIONS IN TELLURIUM HEXAFLUORIDE CLUSTERS

As an example, we have applied this group-theoretical approach to determine the nature and factors of Eq. (17), stimulating the phase changes of a cluster of 59 TeF₆ molecules, and we have compared the results to those from simulations.¹⁰⁻¹² Let us recall that 59 molecules ensure that the interior [Eq. (15)] molecules in the cluster all have the eight neighbors required for a bcc structure. In Fig. 1 we show 12 interior molecules with their orientations: one is in the center; it has a surrounding cube of eight molecules, and three of the six molecules are located in the bodies of the

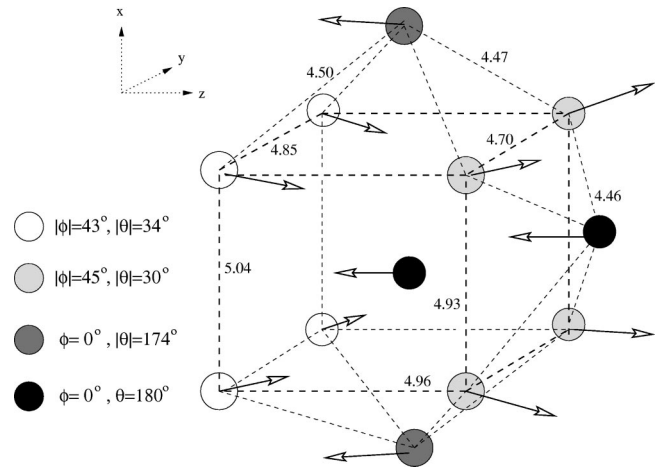


FIG. 1. The interior 12 molecules of 59-molecule cluster, in the vicinity of a phase transition found in the molecular-dynamics simulation (Ref. 10). The arrows indicate the space (θ, ϕ) orientation of one of the molecular axes of symmetry. It is seen that distances between the molecular centers of masses are almost the same but still somewhat different: in the bulk the behavior is the same. This is the reason we call such materials “plastic.”

neighboring cubes. The data are taken from molecular-dynamics simulations¹⁴ at constant temperature. This is a molecular configuration just below the first solid-solid transition, taking the cluster from orientationally disordered body-centered-cubic to a partially ordered monoclinic structure. “Partially” means that the molecules are aligned with respect to only one of the three molecular axes of symmetry. The black and dark gray molecules are almost aligned, as is the case with white and light gray molecules. Further, below this temperature, ~ 76 K, the displacements of the molecular center of masses couple to the orientation changes, inducing rotation-translation interaction. With a still further decrease of the temperature, the cluster becomes almost rigid, the molecular centers undergo very small displacements, and rotation-rotation interaction dominates the second structural transition, which consists of continuous rearrangement and a full ordering of the molecular axes of symmetry. The values of the relevant contributions to the interaction potentials are given in a following paragraph.

We compare the rotation-rotation contributions [Eq. (11)], with their translation-rotation counterparts [Eq. (15)], for the interaction of a TeF₆ molecule with its nearest neighbors located at cubic and at monoclinic sites. For this purpose, we determine the crystal field [Eq. (14)], and the rotational matrix [Eq. (12)]. The CERN Library²⁹ is used to compute the elements of Eq. (12).

Here we give as example the values of the first two terms of the expansion. For octahedral TeF₆, the form factors are $g_0 = (N_a)(4\pi)^{-1/2} = 1.98$, $g_4 = 1.29$ in an O_h environment and $g_4 = 3.88$ in a C_{2h} environment.

The $l=0$ value of S is $(4\pi)^{-1/2}$. The $l=4$ manifold of this system reduces to representations A_{1g} , E_g , T_{1g} , and T_{2g} under $G \equiv O_h$ and to representations $5A_g$ and $4B_g$ under $G \equiv C_{2h}$.

For the normalized function S_4^T we find in O_h ,

$$\alpha_4^{m\tau} = [0.763, m=0; 0.457, m=\pm 4] \quad \text{for } O_h, A_{1g}, 1, 1,$$

$$\alpha_4^{m\tau} = [0.645, m=0; -0.541, m=\pm 4] \quad \text{for } O_h, E_g, 1, 1,$$

$$\alpha_4^{m\tau} = [-0.707, m=\pm 2] \quad \text{for } O_h, E_g, 2, 1,$$

$$\alpha_4^{m\tau} = [-i0.663, m=\pm 1; -i0.25,$$

$$m=\pm 3] \quad \text{for } O_h, T_{1g}, 1, 1,$$

$$\alpha_4^{m\tau} = [\pm i0.663, m=\pm 1; -i0.25,$$

$$m=\pm 3] \quad \text{for } O_h, T_{1g}, 2, 1,$$

$$\alpha_4^{m\tau} = [\pm i0.707, m=\pm 4] \quad \text{for } O_h, T_{1g}, 3, 1,$$

$$\alpha_4^{m\tau} = [\pm i0.663, m=\pm 3; \pm i0.25,$$

$$m=\pm 1] \quad \text{for } O_h, T_{2g}, 1, 1$$

$$\alpha_4^{m\tau} = [\pm 0.663, m=\pm 3; \pm 0.25, m=\pm 1] \quad \text{for } O_h, T_{2g}, 2, 1,$$

$$\alpha_4^{m\tau} = [\pm i0.707, m=\pm 2] \quad \text{for } O_h, T_{2g}, 3, 1.$$

In a C_{2h} environment, all coefficients α^τ are 1 for the five-fold representation A_g ($m=0, \pm 2, \pm 4$) and for the fourfold representation B_g ($m=\pm 1, \pm 3$).

The contribution to the rotational-rotational matrix is the largest for $l=l'=4$. In a cubic symmetry environment the matrix is quasidiagonal, while in C_{2h} surrounding the matrix is diagonal (only one-dimensional representations).

We correlate O_h and C_{2h} in two steps: first, we pass from O_h to D_{4h} , and then use the inferred table for D_{4h} to go on to C_{2h} .¹⁶ Another two-step correlation is also possible: O_h to D_{3d} to C_{2h} . Different possibilities are realized in different structures observed in the experiments with tellurium clusters³ at low temperatures. In a recent paper,³⁰ structural studies of ferroelectric $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ showed the metastability of different phases as a result of changes in the composition x of Ti in the substance, which is a confirmation of our general prediction based on the symmetry considerations.

The coefficients v^R , necessary to compute the crystal field [Eq. (14)], are calculated from Eq. (9) with $p=0$. The cubic symmetry value is $v_{O_h}^R = -7.98$ in the approximation including only the nearest eight neighbors. For the monoclinic structure, C_{2h} , this coefficient is $v_{C_{2h}}^R = -0.61$.

In the approximation of only nearest-neighbor interactions, we determine the energy per molecule: in O_h , the rotation-rotation interaction energy is 4 meV and the translation rotation is 0.3 meV. In C_{2h} , these values are 0.18 and 0.002 meV, respectively. The conclusion is that the translation-rotation interaction can be neglected in the ordering of molecules on monoclinic sites, so that the lower-temperature transition is entirely driven by rotational ordering, and that the transition is continuous even in small systems. However, on cubic sites, motions of the molecular centers of mass are large enough, and the transition is orientation-displacive first-order-like (with two local minima in the free energy), at least in small systems. The highly

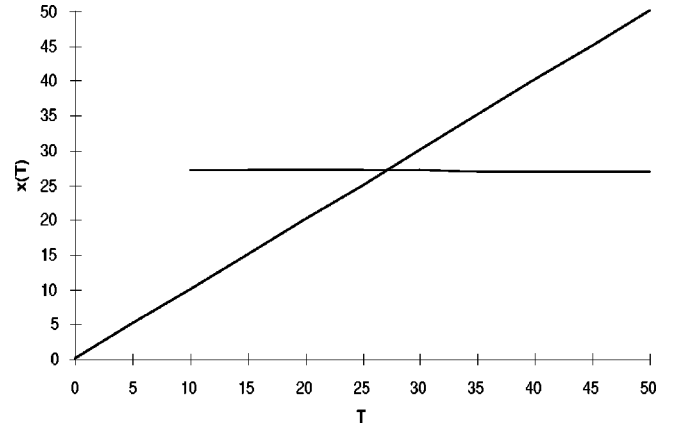


FIG. 2. Temperature dependence of the single-molecule susceptibility (multiplied by the temperature) $x(T)$ of Eq. (19). The temperature is in K.

degenerate state of an O_h molecule in an O_h environment is resolved by a distortion of the cluster structure if the model requires rigid molecules. Thus we can think of the process as a Jahn-Teller effect that distorts the cluster from its local O_h symmetry to C_{2h} via D_{3d} or D_{4h} . The large value of the rotation-rotation interaction leads to a distinct partial ordering of the molecules.¹¹ The transition from O_h to C_{2h} is resolved by invoking the representation of E_g in D_{4h} (or in D_{3d}), equivalent to a splitting of a degenerate mode.

Having the interactions and the total field, we can calculate the free energy F of each phase as a function of the rotator functions considered as order parameters,²⁵

$$F = 0.5 \sum_q [\hat{1} \chi_0^{-1} + \mathcal{F}[\hat{J}]] \delta_\mu(q) \delta_{\mu'}(-q), \quad (18)$$

where $\mathcal{F}(\hat{J})$ and $\delta_\mu(q)$ are the Fourier images of the rotator matrix \hat{J} and $\Delta_\mu(\omega)$, respectively; $\hat{1}$ is the 3×3 unit matrix; and $\chi_0 \equiv xT^{-1}$ is the single-molecule orientational susceptibility,¹⁷

$$x = Z^{-1} (g_4^{A_{1g}})^2 \int \exp[-V^R(\omega)/T] [\Delta_\mu(\omega)]^2 d\omega, \quad (19)$$

with $Z = \int \exp(-V^R/T) d\omega$ the partition function. The expectation value of x does not depend on the components of the rotator function Δ . Its temperature dependence is given in Fig. 2 for the sample cluster considered below.

Two phases of clusters coexist in equal amounts or with equal frequency when their free energies are equal. In the limit of $N \rightarrow \infty$, a phase transition occurs at T_{eq} , which is the point where an eigenvalue of $[\hat{1}T + x(T)\mathcal{F}[\hat{J}]$ vanishes. The temperature dependence of x is very weak, which means that the Curie-Weiss law $\chi_0 = x(T)/(T - T_c)$ is valid for negative diagonal elements of \hat{J} . The transition point T_{eq} occurs at the largest value of the matrix for the representations allowed by the symmetry of the system, i.e., $T_{eq} = \max[-x\hat{J}]$.

The rotation-rotation interaction in the total potential [Eq. (17)] for the orientational ordering in C_{2h} gives the graphical solution for $T_{eq} = \max[-x\hat{J}] = 27$ K for the lower-

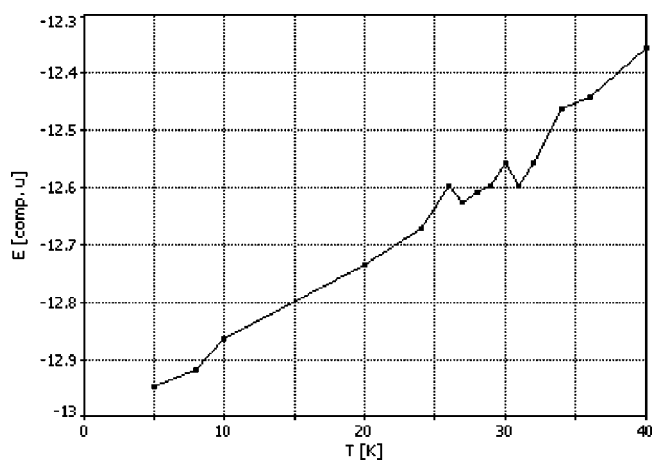


FIG. 3. Caloric curve from canonical Monte Carlo simulations of a 59-molecule TeF_6 cluster; 1 comp. unit is about 1 eV. The calculation uncertainties are 0.02–0.05 comp. units.

temperature transition (Fig. 2). We have implemented the cubic rotator functions $\Delta_l^{A_{1g}}$ in calculating the crystal field [Eq. (14)]. This prediction of the transition temperature is in a good agreement with the results (~ 30 K) from the canonical Monte Carlo simulations,³¹ (Fig. 3), and molecular-

dynamics calculations.¹⁰ This means that the cubic rotator functions [Eq. (14)] are suitable order parameters to describe the mechanism of structural phase changes.

V. CONCLUSION

To summarize, we have shown how the near-neighbor intermolecular interactions of a cluster can be cast in terms of local molecular and site symmetry in a manner that accounts for the multistep phase changes that these clusters exhibit. In particular, we have shown how translation-rotation and rotation-rotation interactions enter into the O_h - D_{4h} - $[D_{3d}]$ transition of TeF_6 to yield a phase change with two local free-energy minima for the small system, but only rotation-rotation interactions enter into the lower-temperature phase change from partial to complete orientational ordering of the molecules on a monoclinic lattice, a change that, according to all indications, involves only a single local free-energy minimum.

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