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On the Relative Stability of Ordered, $F\bar{4}3m$, and Disordered, $Fm3m$, Adamantane Crystals

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Abstract

Atom–atom calculations show that $Fm3m$, $F\bar{4}3m$, and $I\bar{4}3m$ adamantane crystals are close in free energy at room temperature. While $Fm3m$ is stablest for an unstrained crystal, a small (~3%) uniform tetragonal distortion stabilizes an orientationally ordered, strained $I\bar{4}3m$ or $F\bar{4}3m$ structure. The structures may well also be stabilized in a crystal of small mosaic block size in which there is a wide distribution of local tetragonal strain about a mean unstrained value.

Introduction

Recent X-ray diffuse scattering experiments (Reynolds, 1978) have shown that adamantane crystals in which the molecules are orientationally ordered ($F\bar{4}3m$) can be prepared by annealing. Although X-ray Bragg scattering experiments (Nordmann & Schmitkons, 1965) did not distinguish between $F\bar{4}3m$ and the orientationally disordered phase ($Fm3m$) (Reynolds, 1978), both incoherent (Lechner & Heidemann, 1976) and coherent (Damien & Fouriet, 1979; Windsor *et al.*, 1978) neutron scattering experiments on more perfect crystals showed them to be disordered. This communication presents some calculations which elucidate these observations.

Energies of unstrained crystals

One may construct three cubic, face-centred, adamantane phases. $Fm3m$, in which each site is randomly occupied by either of two molecular orientations (differing by inversion); $F\bar{4}3m$, each site being occupied by a molecule of the same orientation and '$P\bar{4}3m$', in which successive *ab* layers have different molecular orientations (illustrated in Reynolds, 1978, Fig. 1). Each of these three phases can distort tetragonally by rotating the molecules around [001], either all in the same sense or successive *ab* layers in alternating senses to give a further six crystal structures. We calculated the energy and crystal structures using the atom–atom model previously used for adamantane (Reynolds, 1975). The results are shown in Table 1, in three groups of three. Each group of three is the basic cubic phase with the two tetragonal phases derived from it by molecular rotation. We should note that a tetragonal distortion of $F\bar{4}3m$ to $P\bar{4}$ if taken far enough can give a cubic phase again ($I\bar{4}3m$).

Taking into account the uncertainties of about 5 kJ mol^{-1} inherent in such calculations where the orientation does not change greatly (Munowitz, Wheeler & Colson, 1977), we estimate the relative enthalpies as

$$F43m > Fm3m > P\bar{4}2_1c \simeq I\bar{4}3m.$$

We cannot order $I\bar{4}3m$ relative to $P\bar{4}2_1c$ since here the possible errors are large (>10 kJ mol^{-1}) because intermolecular interactions change greatly between the two phases, which differ in relative molecular orientation by 45°. All the cubic phases are unstable with respect to small tetragonal distortions if we neglect entropy. For example, $Fm3m$ is stabilized at high enough temperatures by a mechanism exactly analogous to the disordering in a typical displacive transition.

We estimated the crystal structures which molecules interacting with the theoretical potential would adopt at 300 K using the data in Table 1 and estimated

Table 1. *Energy and structure at calculated energy minima for different adamantane crystal symmetries*

	a (Å)	c (Å)	Θ (°)	E (kJ mol^{-1})
$Fm3m$	9·22	9·22	0	−65·4
$P\bar{4}2m$	9·28	9·02	11·6	−66·5
$P\bar{4}$	9·21	9·22	3·5	−65·6
$F\bar{4}3m$	9·43	9·43	0	−58·1
$P\bar{4}n2$		minimum at $F\bar{4}3m$		
$P\bar{4}(\equiv I\bar{4}3m)$	9·83	6·97	45·0	−89·1
'$P\bar{4}3m$'	8·95	8·95	0	−79·8
$P\bar{4}2_1c$	9·83	7·4	17	−81·0
$P\bar{4}$		minimum at '$P\bar{4}3m$'		

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Table 2. *Energies and structure at* 300 K *calculated for various adamantane crystal symmetries*

	a (Å)	c (Å)	$\bar{\Theta}_z$	ΔE (kJ mol^{-1})	ΔG
$Fm3m$	9·69	9·69	0	0	0
$F\bar{4}3m$	9·74	9·74	0	+2·7	+5·9
$P\bar{4}2_1c$	9·81	9·26	9	−3·6	+3·3
$I\bar{4}3m$	10·80	7·63	45	−5·3	−4·0

expansion coefficients (5×10^{-4} K^{-1}). Experimental expansion coefficients and volume changes on phase change were used as guides (Reynolds, 1975, Table 1). The calculated cell dimensions, given in Table 2, are larger than the experimental values for $Fm3m$ and $F\bar{4}3m$ (both 9·43 ± 0·03 Å at 300 K). This is often seen when using potentials derived from 'thermally averaged' data.

Although in this structure the crystal cohesive energies may be readily estimated, the relative entropies cannot. This is because the dispersion of phonons is much greater in $F\bar{4}3m$ and $I\bar{4}3m$ than in $Fm3m$ and $P\bar{4}2_1c$. A cell model is therefore inaccurate, while the extreme anharmonicity of some 'phonons' renders a phonon summation over the Brillouin zone also inaccurate. Nevertheless, we used a cell model (Pertsin & Kitaigorodskii, 1976) to obtain the free energies (relative to $Fm3m$) given in Table 2, which are all very similar, differing by only ~5 kJ mol^{-1}. The 'phonon' entropy change terms are small (~5 kJ mol^{-1}). Separating the entropy into a 'harmonic' part (using only the force constant given by the quadratic terms in the potential) and an 'anharmonic' correction (using quartic term in the potential) (Maradudin & Fein, 1962) shows that the 'anharmonic' term tends to cancel the 'harmonic' term. The main systematic error rests in the enthalpy calculations.

Energies of tetragonally strained crystals

We repeated these calculations at different tetragonal strains, T, $\{=[a - (a^2c)^{1/3}]/(a^2c)^{1/3}\}$ while maintaining a constant volume. The resulting enthalpy calculated is shown in Fig. 1. A positive tetragonal distortion strongly favours the $I\bar{4}3m$ structure. The $F\bar{4}3m$ and $I\bar{4}3m$ derived structures may be interconverted merely by a rotation of the molecules around [001]. This means that there will be a ferrodistortive phase transition between the two at a T of about 2%. We have plotted for $T = 0$ and +2% the potential curves for a $\mathbf{q} = 0$ rotational motion about [001] and [100]; in Fig. 2(*a*) for the $F\bar{4}3m/I\bar{4}3m$ structures and in Fig. 2(*b*) for $Fm3m$. At about T = 2–3%, the rotational mode around [001] has two minima at 45 and ±20°, associated with the $I\bar{4}3m$ structure and the $F\bar{4}3m$ structure respectively. The barrier is of the order of kT. We can describe a transition occurring *via* a softening

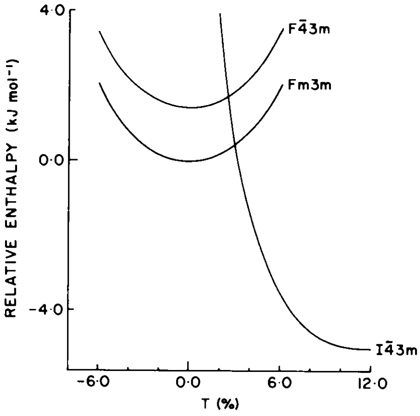
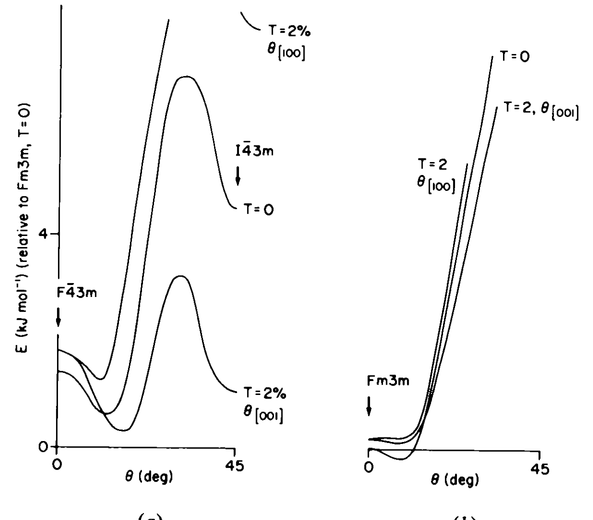


Fig. 1. The dependence of enthalpy on tetragonal distortion for different adamantane crystal symmetries.



(*a*) (*b*)

Fig. 2. Energy coordinates for molecular rotation about [001], Brillouin zone centre mode, at 0 and +2% tetragonal distortion. (*a*) Ordered phases ($I\bar{4}3m$ and $F\bar{4}3m$), (*b*) disordered phase ($Fm3m$).

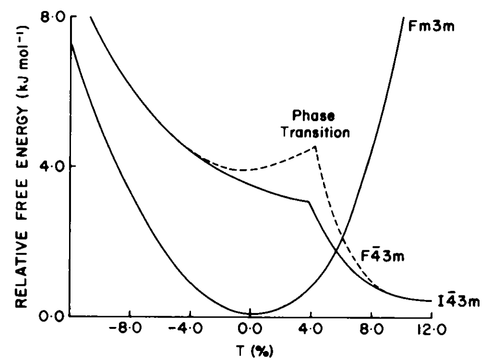


Fig. 3. The variation of free energy with tetragonal distortion at room temperature.

mode at $\mathbf{q} = 0$, with rotational eigenvector around [001]. This softening at $\mathbf{q} = 0$ (which we observed in the X-ray diffuse scattering from our crystal) also causes an increase in total crystal entropy. We illustrate the free energy at room temperature in Fig. 3. The details of the figure are drawn quite arbitrarily. The $I\bar{4}3m$ free energy is drawn higher than $Fm3m$, to accord with experimental observation. The difference between the dotted and solid $F\bar{4}3m \rightarrow I\bar{4}3m$ curve is the notional entropy effect of the phonon softening.

Application to real adamantane crystals

(*a*) *Solution or vapour grown crystals*

An $Fm3m$ crystal is calculated to undergo a phase transition at 300 K to an ordered phase at a few percent positive tetragonal distortion. This phase may be best described as strained $F\bar{4}3m$, in which case there will be a second transition (with $\bar{\Theta}_z$ changing from ~0 to 45°) to strained $I\bar{4}3m$; or the transition may be direct to an $I\bar{4}3m$ phase. Only $Fm3m$ phases have been observed in unstrained systems (Lechner & Heidemann, 1976; Damien & Fouret, 1979; Windsor *et al.*, 1978).

(*b*) *Crystals grown by annealing*

The above cannot explain the observation of $F\bar{4}3m$ in our annealed crystal (Reynolds, 1978) since we measure $T = 0 \pm \frac{1}{2}\%$. However, our crystal had a large measured mosaic spread (6°) about *one axis only* ([001]) due to the growth in a tube and was optically uniform.

We may surmise that polygonization of the crystal, initially saturated with dislocations along [001] (density $\sim 10^{15}$ m^{-2}), to give a block size of diameter ≤ 300 molecules, occurs. The maximum size is dictated by the optical uniformity of the crystal. Each block would be defined by an array of ≤ 60 dislocations around its boundary. Such a small number would ensure substantial local tetragonal strain, of the order of 7% near the block boundary. This defect structure is compatible with our observations.

There are three possibilities for the structure of the crystal – all $Fm3m$, all $F\bar{4}3m$, or mixed $Fm3m$ (in regions of low T) and $F\bar{4}3m$ (in regions of high T). The pure phases will be stable if the correlation range of clusters of the other phase is at least comparable with the block size, if not, the two-phase system will be stable. Qualitatively, we can say that if the free-energy difference between the two phases is small, as it is, then the correlation range may be large enough to stabilize a single phase. The stable phase will be that which has the lowest free energy, given approximately by an averaging of the free-energy curves (Fig. 3) over the distribution of local tetragonal strain. While $Fm3m$ is favoured at $T \leq 0$, it is strongly disfavoured at high T. Therefore, a crystal including regions of large positive tetragonal strain may well adopt an $F\bar{4}3m$ phase. A more definite prediction requires far more knowledge of the crystal's imperfections and the thermodynamics of the pure phases.

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Gyrotropy: An Implicit Form of Ferroicity

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Abstract

Some optically active ferroic crystals (a few ferroelectrics and one ferroelastic) are known to exhibit reversal of the sign of spontaneous optical rotation in certain directions when a suitable electric field or uniaxial stress is applied. This phenomenon, to be called gyrotropy, is examined in the framework of Aizu's

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