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Group theoretical description of phase transitions in solid bromoform

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Abstract. A systematic description of the observed phase transitions in bromoform (CHBr_3) is given. From the symmetry and structures of the α , β , γ phases, the primary order parameters for the transitions are selected. By using induced representations and projection operator techniques, detailed microscopic distortions consistent with the symmetry and structural changes are obtained. To describe the transitions it is necessary to couple representations. Secondary order parameters for the transitions are discussed. Invariant free energy forms containing the primary and secondary order parameters are presented. Using numerical methods, the free energy is minimised and a phase diagram is obtained. Thus both microscopic modes and macroscopic thermodynamics are obtained for the bromoform structural transitions.

1. Introduction

Bromoform, CHBr_3 , is a representative of a series of fairly simple molecular crystals which are methane derivatives. It is one of the solid haloforms, which are made up of molecular units of the type CHX_3 where $\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I . These rigid molecules possess a permanent dipole moment. Methane, from which the haloforms are derived, is known to have disordered (plastic) phases and one expects disordered solid phases along with reorientation phases in the haloforms as well. The series of haloform solids has been studied by x-ray and neutron diffraction (Fourme and Renaud 1966, Kawaguchi *et al* 1972, Myers *et al* 1983, Iwata and Watanabe 1974), Raman and infrared spectroscopy (Anderson *et al* 1985, Burgos *et al* 1981, Sidorov *et al* 1982), dielectric measurements (Sharma *et al* 1979), calorimetric measurements (Valentine *et al* 1962, Sharma *et al* 1979, Burgos *et al* 1981, Boerio-Goates and Woodfield 1988) and nuclear magnetic resonance (Gallier *et al* 1985).

Bromoform has been the haloform most studied in recent years. Raman and infrared experiments (Burgos *et al* 1981) as well as x-ray (Kawaguchi *et al* 1972) and neutron diffraction studies (Myers *et al* 1983) have clearly determined three crystalline phases of bromoform: α , β and γ . The high-temperature α phase is dynamically disordered with two molecules per unit cell and has an average space group symmetry of $\text{P6}_3/\text{m}$ (C_{6h}^2). The dipolar alignment of the molecules along the c axis is disordered with each dipole moment (C_3 axis) pointing either parallel or antiparallel to the axis. The α phase is stable from the melting temperature down to approximately -5°C (Burgos *et al* 1981). The β phase has space group symmetry $\text{P}\bar{1}$ (C_i^1) and is stable from -5°C down to the lowest temperature at which bromoform has been studied. The γ

phase has symmetry $P\bar{3}$ (C_{3i}^1) and is a metastable phase formed by rapid cooling of liquid CHBr_3 to liquid nitrogen temperature. The γ phase transforms irreversibly to the stable β phase by annealing at temperatures above -80°C .

In this paper we give a systematic description of the transitions in bromoform using group theoretical methods. We introduce the formal order parameters for the transitions, specifying appropriate Brillouin zone points and the selected irreducible representations. We determine the order parameters by referring to detailed microscopic 'distortions' and macroscopic strains observed in the transitions and by using induced representations and projection operator techniques. We also obtain the secondary order parameters corresponding to each transition. We give the form of the free energy for the primary order parameters with their coupled invariants. Using numerical methods, we minimise the free energy and a phase diagram is obtained. Thus the microscopic description, along with the macroscopic thermodynamics, is given for the observed transitions in bromoform.

2. α - β transition

In figure 1 is shown a slice along the $(1\bar{1}0)$ plane in bromoform in both the α and β phases. (See Myers *et al* 1983 for atomic positions in both phases.) The large circles represent bromine atoms, the medium-sized circles represent carbon atoms, and the small circles represent hydrogen atoms. In the figure, we can clearly see carbon-bromine layers separated by a distance $\frac{1}{2}c$. The hydrogen atoms protrude into the space between these layers. In the disordered α phase, the hydrogen atoms are randomly distributed among those spaces between the layers, and, on the average, each layer is equivalent to every other layer. The disorder is dynamic. Each molecule jumps between two orientations, one with the hydrogen above the plane and one with the hydrogen below the plane.

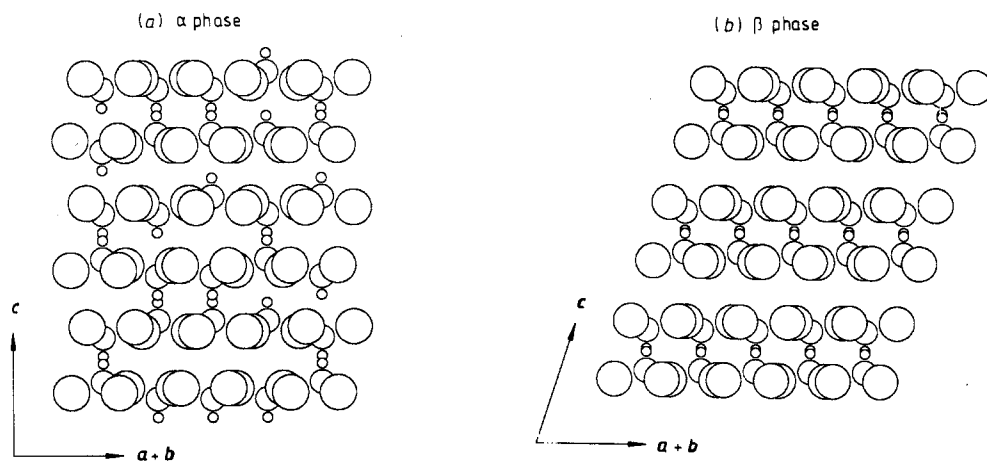


Figure 1. Crystalline structure of bromoform in (a) the α phase and in (b) the β phase. The large circles represent bromine atoms, the medium-sized circles represent carbon atoms, and the small circles represent hydrogen atoms. A slice along the $(1\bar{1}0)$ plane of thickness $a\sqrt{3}$ is shown.

In the transition to the β phase, two main changes take place (Myers *et al* 1983). First of all, the alignment of the bromoform molecules becomes ordered and the hydrogen atoms are now found only between certain layers. Bilayers are formed, consisting of two carbon-bromine layers with a layer of hydrogen atoms in between. Second, the bilayers slip along the $a + b$ direction, producing a shear strain. The unit cell of bromoform in the β phase is shown in figure 2. Notice that there is no change in content of the primitive cell and no change in origin of the space groups in going to the β phase. The two major distortions of the original hexagonal α phase are clearly visible: (1) the dipole moments of the two molecules point in opposite directions, and (2) the c axis is tilted in the direction, $a + b$ (the angles, $\beta \approx \alpha \approx 81^\circ$).

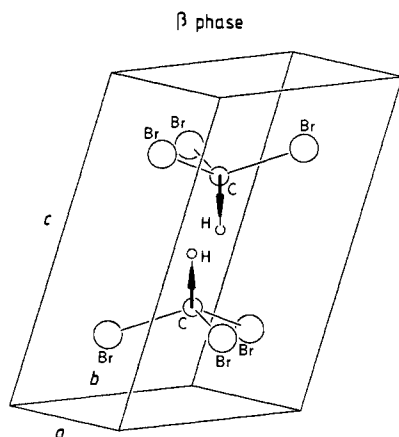


Figure 2. The unit cell of bromoform in the β phase. The arrow shows the direction of the dipole moment of each molecule.

3. Irreducible representations

In order to give a complete group-theoretical description of the α - β transition, it is necessary to first identify the irreducible representations (irreps) of $P6_3/m$ responsible for driving the transition. These irreps must be associated with the Γ point ($\mathbf{k} = 0$) since the size of the unit cell does not change in the transition.

Let us first consider the shear strain. The strain components which cause the c axis to tilt are ϵ_{23} and ϵ_{13} . These transform like the functions, yz and xz . Using tables such as table 4 in Stokes and Hatch (1988), we find that the irrep which has basis functions transforming like yz and xz is the two-dimensional irrep, $\Gamma_4^+ \oplus \Gamma_6^+$. This is the irrep that produces the observed shear strain in the β phase. (This is actually a *physically* irreducible representation, consisting of the direct sum of two irreps which are complex conjugates of each other. We use the irrep labelling of Miller and Love (1967) and Cracknell *et al* (1979)).

The dipole ordering of the bromoform molecules presents a more difficult case. The z component of the dipole moment transforms like the function z . Thus, the representation of the point group at the molecular site must have a basis function that transforms like z . In the α phase, the bromoform molecules occupy the Wyckoff 2(d) positions $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$ with site symmetry $\bar{6}$ (C_{3h}). The irrep of $\bar{6}$ which has a basis function which transforms like z is A_u . Using an induced representation

approach (Hatch *et al* 1987) and referring to the tables of Putnam (1985), we find that both irreps Γ_2^+ and Γ_1^- of $P6_3/m$ are representations induced by A_u at the (d) position. (Alternatively, we can also obtain this information from Kovalev (1986), if we recognise that his irreps τ_2 and τ_7 are Miller and Love's Γ_2^+ and Γ_1^- , respectively. Table 7 in Stokes and Hatch (1988), gives the correspondences between irrep labelling of Kovalev and Miller and Love.)

We have thus found two possible candidates, Γ_2^+ and Γ_1^- , which can produce dipole moments at the bromoform sites in the β phase. They are distinguished by the relative direction of the dipole moments at the two bromoform molecules in the unit cell. We want the irrep which produces these two dipole moments in *opposite* directions. Let us use a projection operator technique to determine this. Both of these irreps are one-dimensional. The matrix representative of the inversion operation is equal to +1 for Γ_2^+ and equal to -1 for Γ_1^- . The inversion operation exchanges the two bromoform molecules in the unit cell and inverts their dipole moments as well. However, the final direction of the dipole moment depends also on the particular representation. The dipole moment is inverted if the matrix representative is equal to +1 and is not inverted if the representative is equal to -1. (The minus sign of the Γ_1^- representative cancels the effect of the inversion operation.) Since the dipole moments of the two molecules are oriented in *opposite* directions in the β phase, Γ_2^+ is clearly the irrep that produces the observed dipole ordering.

At this point, we have identified the irreps which produce the distortions observed in the β phase. Γ_2^+ produces the dipole ordering, and $\Gamma_4^+ \oplus \Gamma_6^+$ produces the shear strain. Since both distortions appear simultaneously at the transition, we consider order parameter distortions (components) of the carrier space of the reducible representation $(\Gamma_4^+ \oplus \Gamma_6^+) \oplus \Gamma_2^+$.

4. Landau theory

The possible symmetries of phases which can be obtained from the order parameter contributions are simply all the isotropy subgroups of $P6_3/m$ for arbitrary vectors transforming according to $(\Gamma_4^+ \oplus \Gamma_6^+) \oplus \Gamma_2^+$. (An isotropy subgroup of $P6_3/m$ is the largest subgroup which leaves a given $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3)$ unchanged.) From Stokes and Hatch (1988), we find that $P6_3/m$ has one isotropy subgroup for irrep $\Gamma_4^+ \oplus \Gamma_6^+$ (i.e. no component from Γ_2^+) and one isotropy subgroup for irrep Γ_2^+ (no component from $\Gamma_4^+ \oplus \Gamma_6^+$). These are $P\bar{1}$ (C_1^1) and $P\bar{3}$ (C_{3i}^1), respectively. Normally, consideration of two representations also produce additional isotropy subgroups. For the case, $(\Gamma_4^+ \oplus \Gamma_6^+) \oplus \Gamma_2^+$ (contributions from both irreps), however, the intersection of subgroups just yields $P\bar{1}$ again. Thus, there are only two isotropy subgroups for $(\Gamma_4^+ \oplus \Gamma_6^+) \oplus \Gamma_2^+$.

Let us now construct the Landau free energy function. Let η_1 and η_2 be the components of the order parameter associated with the two-dimensional irrep $\Gamma_4^+ \oplus \Gamma_6^+$, and let η_3 be the component of the order parameter associated with the one-dimensional irrep Γ_2^+ . The vector $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3)$ spans the three-dimensional representation space of $(\Gamma_4^+ \oplus \Gamma_6^+) \oplus \Gamma_2^+$. When $\boldsymbol{\eta} = 0$, we obtain the α phase, $P6_3/m$. Nonzero values of $\boldsymbol{\eta}$ yield the two isotropy subgroups: $P\bar{3}$ for $\boldsymbol{\eta} = (0, 0, \eta_3)$ and $P\bar{1}$ for $\boldsymbol{\eta} = (\eta_1, \eta_2, \eta_3)$.

The Landau free energy expanded in powers of η_1, η_2, η_3 is given by

$$\begin{aligned} \Phi = & a_1(\eta_1^2 + \eta_2^2) + a_2(\eta_1^2 + \eta_2^2)^2 + a_3(\eta_1^2 + \eta_2^2)^3 + b_1\eta_3^2 + b_2\eta_3^4 + b_3\eta_3^6 \\ & + c_1(\eta_1^2 + \eta_2^2)\eta_3^2 + c_2\eta_1\eta_3(\eta_1^2 - 3\eta_2^2) + c_3\eta_2\eta_3(\eta_2^2 - 3\eta_1^2). \end{aligned} \quad (1)$$

The two sixth-degree terms have been added for stability and do *not* represent all of the possible sixth-degree invariant polynomials possible in the free energy.

To find the possible stable phases of this system, we must minimise this function. First, let us introduce a change of variables

$$\begin{aligned}\eta_1 &= \eta \cos \phi \sin \theta \\ \eta_2 &= \eta \sin \phi \sin \theta \\ \eta_3 &= \eta \cos \theta\end{aligned}\quad (2)$$

We obtain

$$\begin{aligned}\Phi &= \eta^2(a_1 \sin^2 \theta + b_1 \cos^2 \theta) + \eta^4(a_2 \sin^4 \theta + b_2 \cos^4 \theta + c_1 \sin^2 \theta \cos^2 \theta + c'_2 \sin^3 \theta \cos \theta) \\ &\quad + \eta^6(a_3 \sin^6 \theta + b_3 \cos^6 \theta)\end{aligned}\quad (3)$$

where

$$c'_2 = c_2 \cos \phi (\cos^2 \phi - 3 \sin^2 \phi) + c_3 \sin \phi (\sin^2 \phi - 3 \cos^2 \phi).\quad (4)$$

The only place that ϕ appears is in c'_2 . Thus we can minimise c'_2 independent of the rest of the free energy. Since c_2 and c_3 are arbitrary coefficients, the minimum of c'_2 will in general occur at some general value of ϕ . Once c'_2 has been minimised, it can be treated like a constant in the free energy. Note that the free-energy form in equation (3) is the same as the one treated by Gufan and Larin (1980) except for the addition of the c'_2 term. This new term, as we shall see, has a very important effect on the phase diagram.

5. Phase diagram

We used numerical methods to minimise the function in equation (3). We set $a_2 = a_3 = b_2 = b_3 = 1$ and $c_1 = c'_2 = -3$. The actual choice of numerical values for the coefficients do not affect the result much. We must only be sure that the value of c_1 is negative and large enough in magnitude to produce the desired coupling between η_1, η_2, η_3 . Using these values, we numerically minimised Φ for various values of a_1 and b_1 , assuming, as is usual, that all of the temperature and pressure dependence is contained in those two coefficients. We obtained the phase diagram shown in figure 3. The full curves indicate first-order phase transitions, and the broken lines indicate second-order phase transitions. As usual, the second-order phase transitions can be changed to first-order phase transitions by changing the signs of a_2 and b_2 .

The α phase corresponds to the region where the minimum of Φ occurs at $\eta = 0$. The β phase corresponds to the region where the minimum of Φ occurs at $\eta = (\eta_1, \eta_2, \eta_3)$ with all three components non-zero. These are the two phases we have already discussed.

The γ phase corresponds to the region where the minimum of Φ occurs at $\eta = (0, 0, \eta_3)$. This phase has been observed as a metastable state when bromoform is quenched from its liquid state to the temperature of liquid nitrogen. Only η_3 is non-zero, corresponding to distortions that arise from the irrep Γ_2^+ , namely the ordering of dipole moments. The space-group symmetry of the γ phase is $\text{P}\bar{3}$. A slice along the

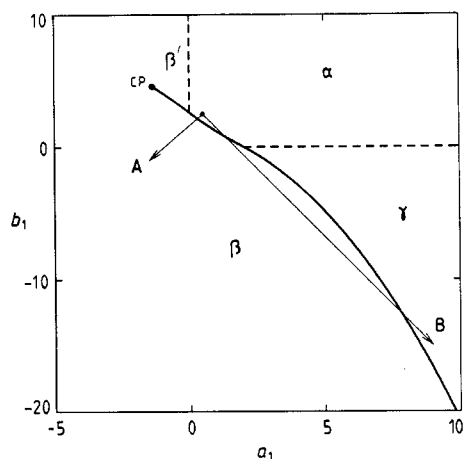


Figure 3. The phase diagram of bromoform. a_1 , b_1 are coefficients in the Landau free energy expansion. The full curve represents a first-order phase transition which ends at a critical point (CP). The broken curves represent second-order phase transitions. Arrow A shows a possible path for the α - β transition observed at -5°C and ambient pressure. Arrow B shows a possible path for the α - β - γ transitions taking place at 10 kbar and 42 kbar under ambient temperature.

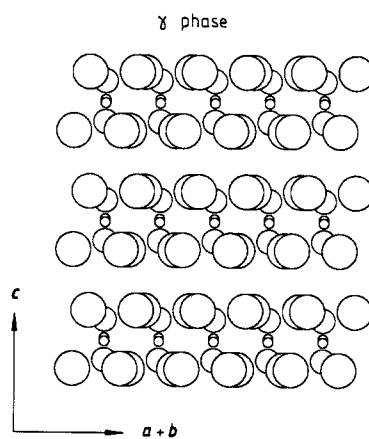


Figure 4. Crystalline structure of bromoform in the γ phase. Compare with figure 1.

($\bar{1}10$) plane in the γ phase is shown in figure 4 (compare with figure 1). As can be seen, the dipole moments are ordered but there is no shear strain as in the β phase.

The β' phase has the same symmetry as the β phase, i.e., none of the three components, η_1 , η_2 , η_3 are zero. However, there is a discontinuous change in the values of η_1 , η_2 , η_3 across the phase line separating β and β' . The discontinuity diminishes in size as we move toward the critical point (CP) and disappears entirely at the critical point. This situation is very much like the critical point which ends the phase line between liquid and gas phases. Such a critical point in a solid has been observed in cerium (Koskenmaki and Gschneider 1978).

Since we do not know the temperature and pressure dependence of a_1 and b_1 , we cannot predict which regions of the phase diagram in figure 3 are physically accessible in bromoform. A possible path taken in the observed α - β transition is shown by arrow A in the figure. The prominence of both the dipole ordering and the shear leads us to believe that the path chosen is representative of the transition. A path going into the β' phase would show nearly negligible ordering while a path going into the γ phase would show no shear. But both are sizeable at the transition. Thus we expect a weakly first order transition. This seems to be consistent with the observed differential scanning calorimetry anomaly (Sharma *et al* 1979) and the small irreversibility of the transition temperature (Myers *et al* 1983).

Note that there is no phase corresponding to $\eta = (\eta_1, \eta_2, 0)$. This phase normally would have appeared where the β' phase is shown (Gufan and Larin 1980), but the $c'_2\eta^4 \sin^3\theta \cos\theta$ term prevents it from ever being stable. The linear dependence on $\eta \cos\theta = \eta_3$ means that the free energy for $\eta = (\eta_1, \eta_2, 0)$ can *always* be lowered by making η_3 slightly non-zero (either positive or negative, depending on the sign of c'_2).

As the β' - α phase line is approached, η_1 and η_2 go to zero like $(-a_1)^{1/2}$, the usual dependence expected at a second-order transition, and η_3 goes to zero like $(-a_1)^{3/2}$. Thus, near the phase line, η_3 goes to zero much faster than η_1 and η_2 , and the crystal structure approaches what we would expect for $\boldsymbol{\eta} = (\eta_1, \eta_2, 0)$. In the case of bromoform, this would be a structure where the shear strain is present without any dipole ordering.

6. Secondary order parameters

Thus far we have mainly considered the major distortions observed in the phase transitions. These are the primary order parameters. There are also many secondary order parameters. Consider the α - β transition. Any distortion allowed by the $\text{P}\bar{1}$ symmetry of the β phase will also appear to some degree at this transition. These are called the secondary order parameters. They are not as predominant as the primary order parameters. For example, the irrep $\Gamma_3^+ \oplus \Gamma_5^+$ produces non-zero strain components, $\epsilon_{11} - \epsilon_{22}$ and ϵ_{12} . Let η_4, η_5 be the components of the order parameter associated with this irrep. Coupling with $\Gamma_4^+ \oplus \Gamma_6^+$ introduces two terms in the Landau free energy which are of the form

$$(\eta_1^2 - \eta_2^2)\eta_4 + 2\eta_1\eta_2\eta_5 \quad (\eta_1^2 - \eta_2^2)\eta_5 - 2\eta_1\eta_2\eta_4.$$

The linear dependence of η_4, η_5 in these terms means that if η_1, η_2 are non-zero (the β phase), then the free energy can *always* be lowered by making η_4, η_5 slightly non-zero. Thus, non-zero (η_4, η_5) must be present to some extent. Even though these strain components are less evident than $\epsilon_{13}, \epsilon_{23}$ in the β phase, symmetry requires that they be present nonetheless. $\epsilon_{11} - \epsilon_{22}$ and ϵ_{12} are secondary order parameters. ϵ_{13} and ϵ_{23} are primary order parameters.

Similarly, $\Gamma_3^+ \oplus \Gamma_5^+$ also produces a distortion at the bromoform molecules that transforms like x and y . For example, x and y components of the dipole moment will appear in the β phase, even though they may be much smaller than the z component, which is a primary order parameter. Besides components of the dipole moment, molecular displacements transforming like x, y, z will be present. In each case, however, the dipole moment or displacement of one bromoform molecule must be opposite in direction to the dipole moment or displacement of the other bromoform molecule in the unit cell in order to preserve the point of inversion in $\text{P}\bar{1}$.

$\Gamma_4^+ \oplus \Gamma_6^+$ produces distortions at the bromoform molecules that transform like the x and y components of an *axial* vector. These are usually denoted S_x, S_y . In the case of bromoform, this distortion may appear as a rotation of the molecule about an axis in the xy plane. Because of the transformation properties of axial vectors, this distortion must be the *same* for both bromoform molecules in the unit cell in order to preserve the point of inversion in $\text{P}\bar{1}$.

7. γ - β transition

The phase transition from the γ phase to the β phase can also be described by Landau theory. (See Myers *et al* 1983 for atomic positions in the γ phase.) The space group symmetry of the γ phase is $\text{P}\bar{3}$ (C_{3i}^1). There is no multiplication of the primitive cell and

no space group origin change. The primary distortion that takes place in the transition to the β phase is the appearance of the strain components, ϵ_{13} and ϵ_{23} . We find from table 4 in Stokes and Hatch (1988) that the irrep $\Gamma_2^+ \oplus \Gamma_3^+$ has basis functions that transform like xz and yz . This must be the irrep that drives the transition. We find in table 1 of Stokes and Hatch (1988) that there is one isotropy subgroup of $P\bar{3}$ for this irrep. It is $P\bar{1}$, the β phase.

The Landau free energy function expanded to fourth degree in the order parameter is given by

$$\Phi = a_1(\eta_1^2 + \eta_2^2) + a_2(\eta_1^3 - 3\eta_1\eta_2^2) + a_3(\eta_2^3 - 3\eta_2\eta_1^2) + a_4(\eta_1^2 + \eta_2^2)^2 \quad (5)$$

where η_1, η_2 are now components of the order parameter associated with the irrep $\Gamma_2^+ \oplus \Gamma_3^+$ of $P\bar{3}$. (Note that the coefficients a_i and the order parameter components η_i here have a different meaning from the ones in equation (1).) Because of the presence of the third-degree terms, the transition from the γ phase to the β phase must be first order, in agreement with the phase diagram in figure 3.

Experimentally, an irreversible transition from the γ phase to the β phase is observed if the metastable γ phase is annealed at a temperature above -80°C .

At ambient temperature a sequence of transitions have been observed under pressure (Shimizu and Matsumoto 1984, Zhao *et al* 1986). The α - β transition takes place at ~ 10 kbar and the β - γ takes place at ~ 42 kbar. In this sequence the γ phase is stable. We have indicated a possible path for this sequence of transitions with arrow B of figure 3.

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