Physics – Uspekhi **50** (4) 354 – 358 (2007) © 2007 Uspekhi Fizicheskikh Nauk, Russian Academy of Sciences

ORAL ISSUE OF THE JOURNAL "USPEKHI FIZICHESKIKH NAUK" PACS numbers: **36.40. – c**, 61.46.Bc, 64.70.Dv

Clusters and phase transitions

B M Smirnov

DOI: 10.1070/PU2007v050n04ABEH006235

Abstract. The fundamental problems of cluster physics occupy seventh place in the V L Ginzburg classification of most important problems in modern physics and are discussed below.

Clusters are point 7 in the classification of contemporary physical problems by V L Ginzburg, and this report is devoted to some fundamental aspects of this problem. A cluster consists of identical particles (atoms) which are usually bound in the cluster. Clusters conserve their individuality until they are isolated, and therefore they are used in the form of cluster beams for various applications, including the production of new materials, which is a direction of nanotechnology advancement, and in sources of X-ray radiation and generators of neutrons. Below we discuss only fundamental problems of cluster physics.

Clusters became a separate physical subject in the 1980s when it was established experimentally that solid clusters are characterized by magic numbers of atoms [1]. Various cluster parameters, like the specific binding energy of atoms, the cluster ionization potential, the electron affinity of clusters and some other parameters, as a function of the number of cluster atoms have extrema at magic numbers. We give here only two examples: the mass spectrum of inert atom clusters resulting from free jet expansion of an inert gas (Fig. 1a) [2], and the mass spectrum of photoionization of a magnesium cluster beam (Fig. 1b) [3]. Magic numbers correspond to filled cluster structures, and in the cases under consideration, when clusters have a shell structure, magic numbers relate to the completed atomic shells in these clusters.

Since magic numbers are a property of only solid clusters, the character of cluster mass spectra may be used for determining the cluster melting point if a cluster beam passes through a thermostat (Fig. 2a) [4]. Then, the oscillation structure of the mass spectrum gives evidence of the solid cluster structure, while a continuous mass spectrum corresponds to the liquid state, and the transition between these aggregate states gives the melting point for clusters of a given size (Fig. 2b) [4]. As for cluster size, magic numbers are observed for clusters consisting of up to several thousand atoms [5].

Being a specific physical object, a cluster may be regarded as a model for macroscopic atomic systems. The evolution of

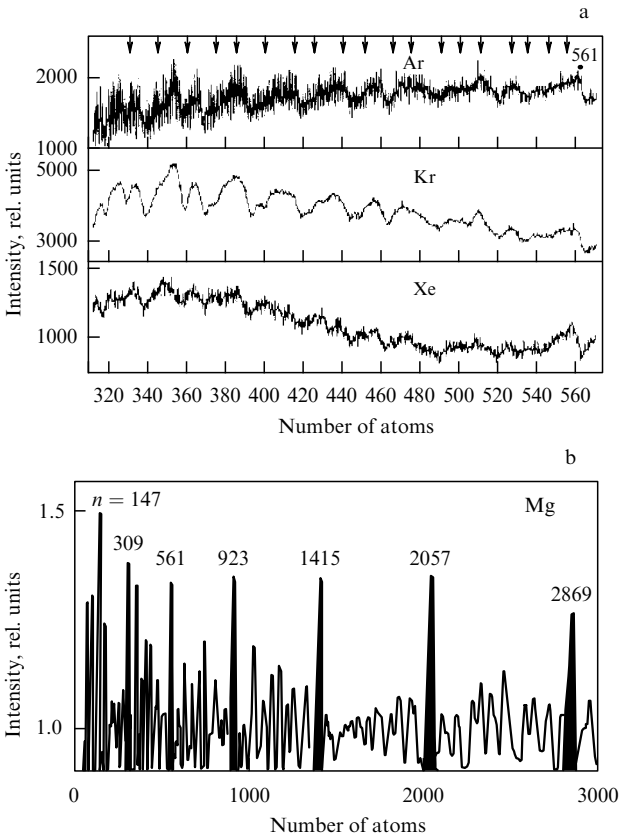

Figure 1. (a) The mass spectrum of inert gas clusters formed as a result of the free jet expansion of inert gases through a nozzle. (b) The mass spectrum of magnesium clusters formed by photoionization of a magnesium cluster beam [2]. Maxima in the mass spectra correspond to completed shells of the icosahedral structure.

clusters with a relatively high excitation energy that produces changes in a configuration of cluster atoms may be described as the displacement of a point along the potential energy surface (PES) in a multidimensional space of atomic coordinates. The principal property of PES, discovered in the 1970s as a result of computer simulation of clusters [6], consists in a large number of local minima of the PES. For example, the PES of the Lennard-Jones cluster involving 13 atoms contains more than 1000 local minima [6, 7], and the number of local minima of the PES increases exponentially with an increase in the number of cluster atoms [8, 9]. This leads to a specific behavior of clusters and complex molecules (including biomolecules), so that an atomic configuration corresponds to a certain local minimum of the PPS over a large time period compared to the typical time of atomic oscillations, and then the transition proceeds to a neighboring local minimum of the PPS through the potential barrier (Fig. 3). This character of cluster evolution is called saddle-

B M Smirnov Institute for High Temperature,
Russian Academy of Sciences,
ul. Izhorskaya 13/19, 127412 Moscow, Russian Federation
Tel./Fax (7-499) 190 42 44
E-mail: bsmirnov@orc.ru

Received 15 November 2006
Uspekhi Fizicheskikh Nauk **177** (4) 369 – 373 (2007)
Translated by B M Smirnov; edited by A Radzig

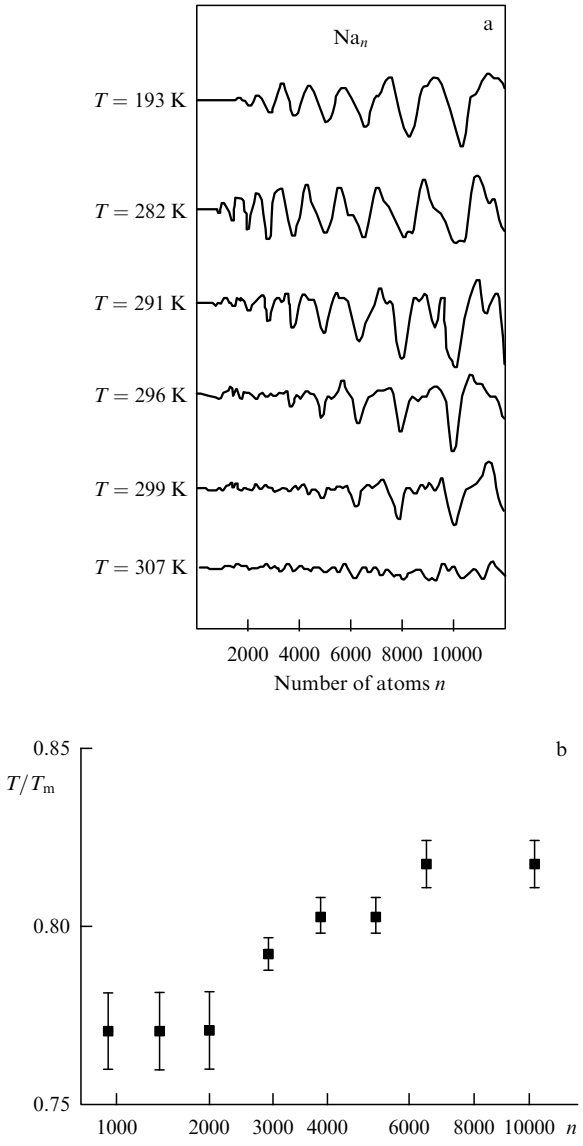

Figure 2. (a) The mass spectrum of sodium clusters which pass through a thermostat maintained at an indicated temperature. (b) The melting point of clusters with respect to the melting point of bulk sodium follows from the data depicted in figure (a).

crossing dynamics and leads to separation of configuration and oscillation degrees of freedom (Fig. 4) [10] that constitutes a general property of atomic systems [11]. Then, the phase transition is connected with transitions between configuration degrees of freedom.

The important cluster peculiarity is the phase coexistence near the phase transition [12], so that the transition between two aggregate states proceeds in some range of the excitation parameter (the cluster temperature in the isothermal case or the excitation energy in the adiabatic case), whereas in the macroscopic case this transition has a jump-like form. The phase coexistence is a property of a system consisting of a restricted number of monomers, and for such a system the difference between the first- and second-order phase transitions is lost. Demonstration of this fact of phase coexistence is given in Fig. 5 [12] and testify to a bimodal distribution of the total kinetic energy of cluster atoms for the Lennard-Jones cluster involving 13 atoms, where the kinetic energy is averaged over fast atomic oscillations.

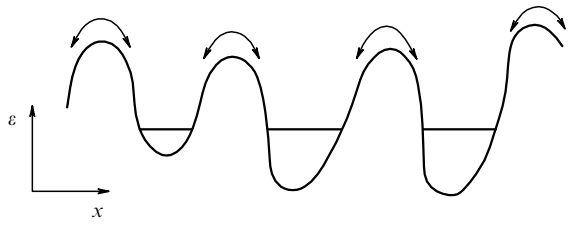

Figure 3. The character of transitions through saddle points in the course of evolution of an ensemble of many interacting atoms.

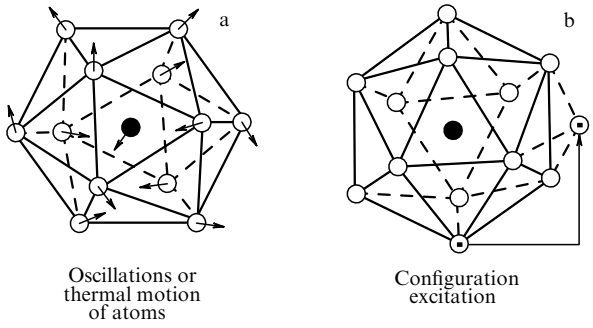

Figure 4. Types of cluster excitations as a result of atomic oscillations (a) and configuration excitation (b) [11].

The character of dynamic phase coexistence is such that a part of time the system is found in one aggregate state, the other part of time it is found in another aggregate state, and a time of location in each aggregate state is large compared to the typical oscillation time of atoms, which is of the order of $1/\omega_D$, where ω_D is the Debye frequency. Dynamic phase coexistence determines some properties of the atomic system near the melting point. In particular, the heat capacity of an isolated cluster as a function of its average temperature that is expressed through the total kinetic energy of cluster atoms can be negative in the phase-transition region [9, 13]. This means that an increase in the excitation energy of an isolated cluster can induce a partial transition of the thermal cluster energy into the energy of configuration excitation.

Note that two aggregate states of a simple atomic system do not follow from general physical laws. Experience gained with clusters shows that in some cases (Lennard-Jones clusters consisting of 8 and 14 atoms) only the solid aggregate state is realized, while several aggregate cluster states may be realized in other cases. The latter is demonstrated in Fig. 6 for a Lennard-Jones cluster involving 55 atoms [14]. Caloric curves of this cluster (Fig. 6) display the existence of the solid and liquid aggregate states in this cluster and the aggregate state that corresponds to the solid core and the liquid shell. By the way, experimental research on bulk systems allows one to separate surface melting from volume melting, since these phenomena are characterized by different temperature regions. Experience accumulated with clusters deepens our understanding of the phase transition in bulk atomic systems and leads to the generalization of the classic thermodynamic definitions for the phase and the phase transition.

One can simplify the description of saddle-crossing dynamics by introducing the elementary configuration excitation — that is, void, and in this way transfer from a dynamic description of a cluster as a system of bound atoms

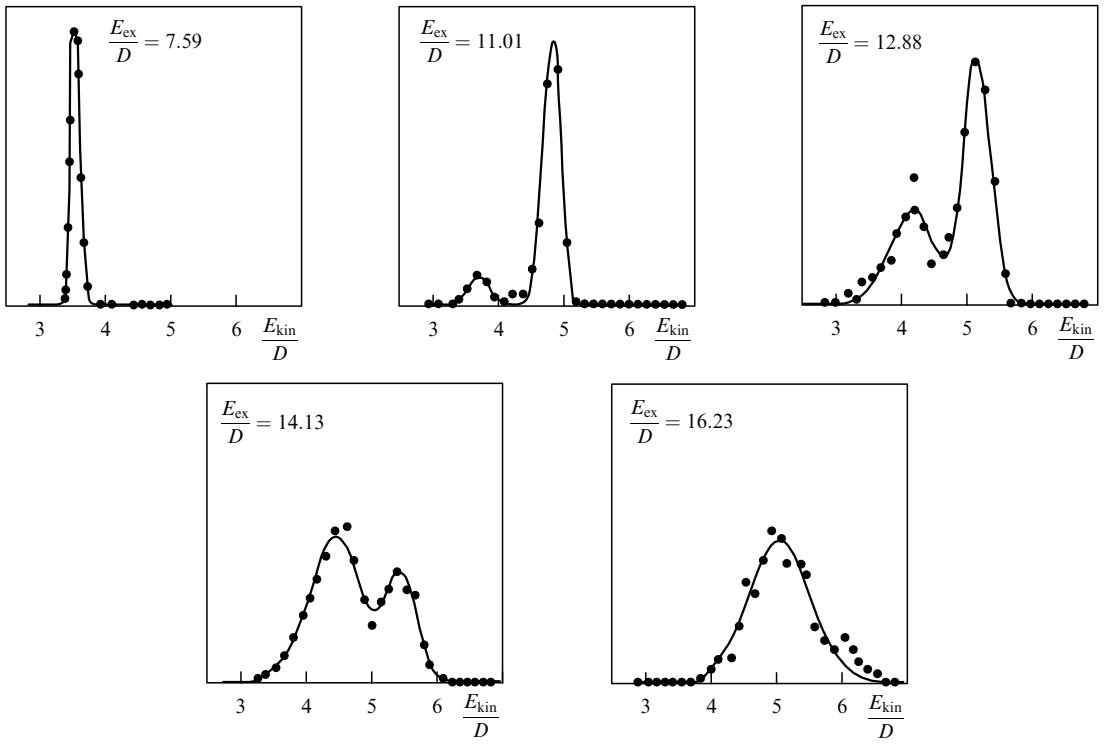

Figure 5. The distribution over the total kinetic energy of cluster atoms for a Lennard-Jones cluster consisting of 13 atoms [12]. Here, E_{ex} is the cluster excitation energy, E_{kin} is the total kinetic energy of atoms averaged over fast atomic oscillations, and D is the binding energy per bond.

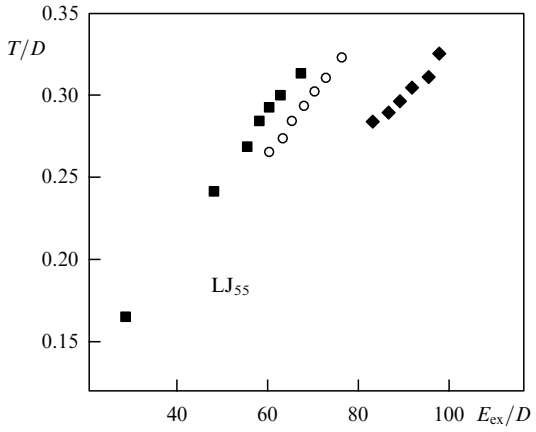

Figure 6. Caloric curves for a Lennard-Jones cluster consisting of 55 atoms [14] for different cluster aggregate states.

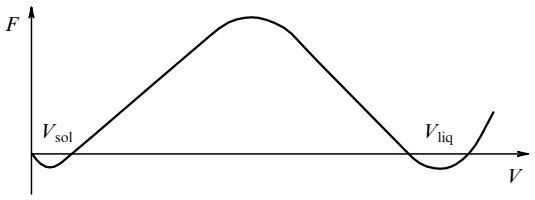

Figure 7. The free energy of an ensemble of interacting atoms as a function of a number of internal voids [17].

to a statistic one [15]. At low excitations, a void corresponds to a perturbed vacancy, and at high excitations a void is a statistical characteristic because its size and shape and the formation energy vary in time, so that we are dealing with average void parameters. From the void standpoint, the liquid – solid transition corresponds to the departure of voids outside the system [16]. In the case of two aggregate states, the free energy of condensed inert gases as a function of a number of voids (Fig. 7) has two minima, solid and liquid, that give rise to the solid and liquid aggregate states, and one of these is the stable state, the other one is the metastable state.

Based on the void concept, we shall consider two aspects of aggregate states. The first one relates to the phase transition criterion. In particular, according to the Lindemann criterion that was established about hundred years ago [18], the amplitude of atomic vibrations at the phase transition is 10 – 15% of the average distance between neighboring atoms. Contemporary criteria of the phase transition, which resulted from the development of computer simulations of clusters, are based on correlations in atomic distributions (see, for example, Ref. [19]). As an example, Fig. 8 illustrates the fluctuation of the square root of the distance between nearest neighbors in a Lennard-Jones cluster consisting of 13 atoms. This quantity has a jump at the melting point. Analyzing the melting criteria, one can obtain the contradiction between the nature of the phase transition that is determined by configuration cluster excitation and the criteria of practice that are based on thermal atomic motion. Since the configuration and thermal degrees of freedom for a cluster are separated, the phase transition cannot result from thermal atomic motion. This paradox can be resolved on the basis of data collected in Table 1, where the entropy jumps at phase transitions are given at zero temperature and the melting point. The entropy of the liquid state as a rarer state varies with increasing temperature more sharply than that of the solid state, and in this part of entropy

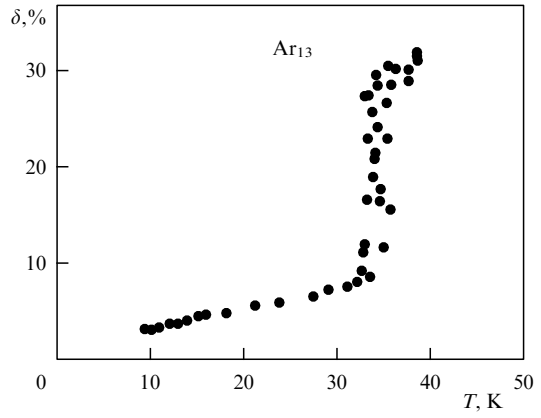

Figure 8. Fluctuations of the square root of the mean distance squared between nearest neighbors of a Lennard-Jones cluster consisting of 13 atoms [19] that are averaged over atoms and fast oscillations.

Table 1. Variation of the specific entropy as a result of melting of the Lennard-Jones clusters consisting of 13 and 55 atoms, and for a bulk inert gas [13].

	ΔS_0	ΔS_m	$\Delta S_0/\Delta S_m$, %
LJ_{13}	5.2	7.9 ± 0.3	66 ± 3
LJ_{55}	31 ± 2	45 ± 2	69 ± 7
Bulk inert gas *	0.73	1.68 ± 0.03	43 ± 1
* ΔS_0 and ΔS_m are the entropy jumps at zero temperature and the melting point, respectively.			

the connection between the phase transition and the thermal atomic motion takes place.

The second aspect of aggregate states corresponds to the formation of glassy states in simple systems of interacting atoms, like condensed inert gases. As follows from Fig. 9b [20], the liquid minimum of the specific free energy of condensed argon disappears at some temperature, the freezing temperature, so that at lower temperatures the metastable liquid state is absent.

Since the liquid–solid phase transition corresponds to the withdrawal of voids outward and the diffusion of voids inside an atomic system assumes an activation character, voids may be frozen inside an atomic system as a result of fast cooling. For a simple bulk atomic system, as condensed inert gases, glassy states may be prepared by two methods: fast cooling of a liquid system or deposition of atoms onto a substrate at a low temperature. In both cases, the system being formed has an amorphous structure, and this glassy state of an atomic macroscopic system or the cluster can pass to the solid aggregate state as a result of heating. Figure 10 exhibits the evolution of bulk argon that is deposited on a target at a temperature of 10 K (the melting point of bulk argon is 84 K) and is subsequently heated [22]. The characteristic of the state is the saturated vapor pressure over the sample. An analysis of the glassy transition (the transition between the glassy and solid states) resulting from sample heating reveals that the parameters of an experimentally examined glassy state and the parameters of a frozen liquid are close.

Thus, the above analysis of some aspects of cluster physics and phase transitions testifies to the fundamental character of the phenomena under consideration.

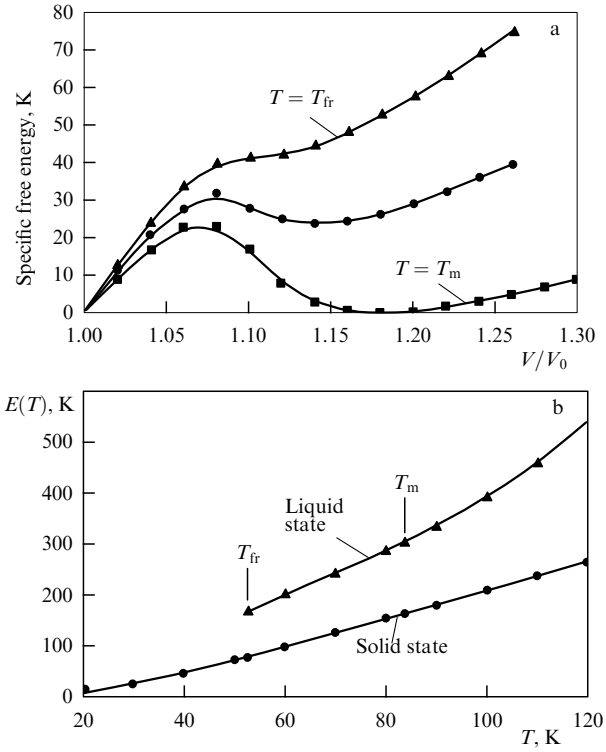

Figure 9. (a) The specific free energy of bulk argon as a function of the volume per atom, resulted from the void model. (b) Caloric curves for bulk argon that follow from the data depicted in figure (a).

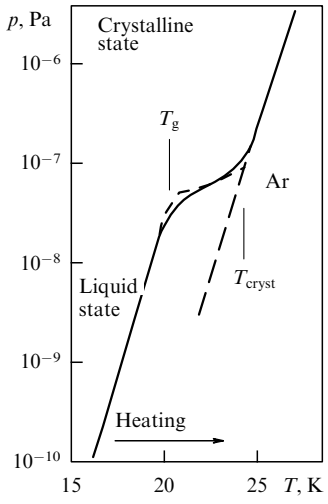

Figure 10. Decay of the glassy state of bulk argon obtained by deposition of argon atoms on a target at a temperature of 10 K [21, 22] (T_g is the temperature of the glassy transition, and T_{cryst} is the crystallization temperature).

This paper was partially supported by the Russian Foundation for Basic Research (grant No. 06-02-16146).

References

1. Echt O, Sattler K, Recknagel E *Phys. Rev. Lett.* **47** 1121 (1981)
2. Miehle W et al. *J. Chem. Phys.* **91** 5940 (1989)
3. Martin T P et al. *Chem. Phys. Lett.* **176** 343 (1991)
4. Martin T P et al. *J. Chem. Phys.* **100** 2322 (1994); Martin T P *Phys. Rep.* **273** 199 (1996)

5. Martin T P et al. *Chem. Phys. Lett.* **172** 209 (1990)
6. Hoare M R, Pal P *Adv. Phys.* **20** 161 (1971); **24** 645 (1975)
7. Komatsuzaki T, Berry R S *J. Chem. Phys.* **110** 9160 (1999)
8. Wales D J et al. *Adv. Chem. Phys.* **115** 1 (2000)
9. Wales D J *Energy Landscapes* (Cambridge: Cambridge Univ. Press, 2003)
10. Vekhter B et al. *J. Chem. Phys.* **106** 4644 (1997)
11. Smirnov B M *Principles of Statistical Physics* (Berlin: Wiley, 2006)
12. Jellinek J, Beck T L, Berry R S *J. Chem. Phys.* **84** 2783 (1986)
13. Berry R S, Smirnov B M *Usp. Fiz. Nauk* **175** 367 (2005) [*Phys. Usp.* **48** 345 (2005)]
14. Kunz R E, Berry R S *Phys. Rev. E* **49** 1895 (1994)
15. Reiss H, Frisch H L, Lebowitz J L *J. Chem. Phys.* **31** 369 (1959)
16. Smirnov B M *Clusters and Small Particles: in Gases and Plasmas* (New York: Springer-Verlag, 2000)
17. Smirnov B M *Zh. Eksp. Teor. Fiz.* **112** 1847 (1997) [*JETP* **85** 1010 (1997)]
18. Lindemann F A *Phys. Z.***11** 609 (1910)
19. Zhou Y et al. *J. Chem. Phys.* **116** 2323 (2002)
20. Berry R S, Smirnov B M *Zh. Eksp. Teor. Fiz.* **120** 889 (2001) [*JETP* **93** 541 (2001)]
21. Gutzow I, Schmelzer J *The Vitreous State: Thermodynamics, Structures, Rheology, and Crystallization* (Berlin: Springer-Verlag, 1995)
22. Kouchi A, Kuroda T *Jpn. J. Appl. Phys.* **29** L807 (1990)