Kinetics of pressure induced structural phase transitions—A review

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Abstract. The current status of experimental as well as theoretical advances in the understanding of kinetics of structural phase transitions is reviewed. A brief outline of the classification of phase transitions and classical ideas in the theory of kinetics of phase change is presented first. High pressure experimental techniques developed for studying the kinetics of structural transitions are reviewed and the salient features of each technique is brought out. The experimental technique using the diamond anvil cell (DAC) and image processing gets special mention as it promises to impart a new direction to this field. The usefulness of kinetic parameters in understanding the mechanism of a phase transition is examined. Typical examples from the literature are provided to give a flavour for these kind of studies. In conclusion, several open questions are raised which could pave way for future work in this area.

Keywords. High pressure; structural transitions; kinetics.

1. Introduction

In this paper, the present status of research on kinetics of structural phase transitions, both experimental and theoretical is reviewed. The cross-disciplinary subject of kinetics of phase transitions is of vital interest to condensed matter physicists. This is not only of academic importance, but also of technological relevance. The literature abounds in experimental studies and, to a lesser extent, in theoretical studies, and the subject is continually growing. Newer topics like amorphization under pressure have rejuvenated the interest in the subject.

This report is written with the perspective of a high pressure physicist and with particular interest in polymorphic transitions under high pressure. For the investigation of the thermodynamic and electronic equilibrium properties, a broad spectrum of methods for pressure generation and physical measurements have been developed (Jayaraman 1983, 1986; Hemley et al 1987; Spain and Pauwwe 1977; Hochheimer and Etters 1991; Singh 1992). The measurement of equilibrium properties, however, gives only incomplete insight into the detailed mechanics of phase changes. The accurate determination of the phase equilibria and phase diagrams becomes harder at low temperatures due to increasing hysteresis effects. Consequently, the extrapolation of the experimental data to zero temperatures and the comparison with quantum mechanical ab initio calculations become questionable. The study of phase transformation kinetics yields data on the reaction velocity and additional information on the basic mechanisms of the transition. This allows a more accurate extrapolation of the phase equilibria to low temperatures (Merkau and Holzapfel 1986; Jeanloz 1987; Kruger et al 1990) and the comparison with theoretical results. In addition, the kinetics of phase changes under pressure is of basic importance for understanding the physical and chemical reactions that control the formation of high-pressure phases with special properties. Therefore a knowledge of the mechanisms of phase transformations is a presupposition for understanding the synthesis of new materials (Lorenz et al 1988). In geological applications, various crystallization processes cannot be studied under laboratory conditions because of long duration of the experiments. The information obtained from natural samples (e.g. igneous rocks) is restricted to the chemical, physical and structural analysis of the end product of series of different kinetic processes, which led to formation of the sample. The application of a kinetic model of phase transition can be useful to investigate more precisely the thermodynamic conditions of rock formation. However, the kinetics of the pressure induced transformations have not been studied as extensively as the kinetics of the temperature induced transformations mainly because of the difficulties in high pressure experiments.

The pressure induced transformations, which have been studied for their kinetic aspects fall under two categories. In the first category are the polymorphic transformations, which are displacive in nature. The transformations usually have low activation energies and are relatively rapid. Since polymorphic transformations can occur at relatively lower temperatures (room temperature or lower), any diffusion process is unlikely to take place. The second category of the transformations is the reconstructive type. These have large activation energy and are generally sluggish. The transformation rates become appreciable only at higher temperatures. Such transformations are often diffusion controlled.

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In § 2, various classification schemes of phase transitions are described. The importance of structural classification schemes and their present level of understanding are briefly discussed. A brief introduction to the world of pressure induced structural phase transitions is given in § 3.

Section 4 is devoted for reviewing the existing understanding on the kinetics of phase transitions from thermodynamics point of view. In addition, some basic and well known theoretical concepts relevant to the subject are reproduced. Various experimental techniques used for studying kinetics are described in § 5. This also includes a section on kinetic studies in a diamond anvil cell (DAC). In § 6, some interesting studies on kinetics of phase transformation, from the literature, are described. The conclusions and the future directions are laid out in § 7.

2. Classifications of phase transitions

This brief section on classification scheme is included to review the status of kinetics as a parameter for classifying phase transitions. The importance and utility of other schemes are discussed for completion sake. Much of the earlier work on ‘classifying’ the changes from one structure to another was based on the rate with which the transition was effected. While crystallographic differences were recognized, a scheme for the classification of the transitions based on the nature of the crystallographic change was in fact the last to be developed. In between these two developments, the well known work of Ehrenfest provided a rigorous treatment of the thermodynamics to the case of transition between two solid phases. Roy (1973) has reviewed these classifications systematically. He has identified four principal approaches to the problem by classifying phase transitions based on kinetic, thermodynamic classification, thermochemical, and structural considerations.

The kinetic classification starts from the early work of Le Chatelier and simply divides transitions into two main groups viz. (i) rapid, or non-quenchable, and (ii) sluggish. However, no real classification scheme can be based on this parameter since it does not treat any basic property of either of the two phases. Moreover, as experimental capabilities grow, what is regarded as ‘non quenchable’ today may be established to be quenchable tomorrow. However, some recent research on this aspect has pointed out that with the right combination of the structural as well as the kinetic aspect an acceptable criterion of classification may emerge.

The thermodynamic classification leads to a very satisfactory conceptual scheme, dividing all phase transitions according to their ‘order’ and is summarized by the statements of table 1. In actual practice, several corollary relations, which are demanded by these elementary relations, are frequently ignored.

Thermochemical classification proposes to classify all transitions by the magnitudes of $\Delta H$ (change in enthalpy) and $\Delta S$ (change in entropy). It was hoped that if a matrix of these two elements is constructed, transitions could be pigeonholed in it. The difficulty arises because of the unavailability/unreliability of the data on $\Delta H$ and $\Delta V$ etc and the extreme rarity of data on $\Delta G$ (coefficient of thermal expansion) and $\Delta K$ (isothermal compressibility). The applicability of this scheme is limited because it does not treat the fundamental differences between the phases.

While the thermodynamic treatment of phase transitions is fundamental and useful, it does not provide a geometrical picture of the microscopic changes accompanying a transition. In fact, the major strides made in the understanding of the crystal chemistry (Rao and Rao 1967, 1978) in terms of atomic arrangements and bonding can be advantageously applied to the study of phase transitions in solids. For example, the new phase obtained after a transition may be related to the parent phase. The transition may have been accompanied by a change in the primary coordination or secondary coordination either being brought out by a reconstructive or displacive mechanism. The transition could be accompanied by a major change in the electronic structure or the bond type. A detailed study of the structures of the parent phase and the transformed phases, particularly looking for the presence of orientational relations between them, becomes important in understanding the mechanism of transition. It is now known that the transition in many solids may involve simple deformational (or orientational) relation between the two phases similar to those in the martensitic transitions common on metal systems. Recently, Gupta and Chidambaram (1994) have studied the symmetry systematics of the pressure induced structural phase transitions and proposed a classification into four categories: iso-symmetric, group–subgroup, intersection group and order–disorder transitions.

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>Thermodynamic classification.</th>
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<tbody>
<tr>
<td><strong>Classification by stability</strong></td>
<td><strong>Classification by order (after Ehrenfest)</strong></td>
</tr>
<tr>
<td>Enantiotropic = Reversible, proceeds in both directions (hence equilibrium attainable)</td>
<td>1st order = Discontinuity in 1st derivative functions of $G$</td>
</tr>
<tr>
<td>Monotropic = Irreversible, proceeds in only one direction (no equilibrium possible between phases)</td>
<td>2nd order = Discontinuity in 2nd derivative of $G$. Change of slope only in 1st derivative property</td>
</tr>
<tr>
<td>Equilibrium = (only requires reversibility)</td>
<td>$n$th order = Discontinuity in the $n$th derivative property of $G$. Change of slope only in $(n-1)$th derivative.</td>
</tr>
<tr>
<td>Metastable = Between two phases neither of which is the lowest $G$ phase</td>
<td>Stable = Between two lowest free energy phase</td>
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