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The Hierarchic Order in the Solid State, Part IV[1]
States of "Optimal Hierarchic Order"
Solid—"Meltlike" Transitions

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An attempt is made to gain an understanding for "unusual" properties of extremely thin films and extremely small grains. Lamelles of gold are known to flow together far below the melting point. Independent from temperature a certain load is found, under which a film of given thickness undergoes neither elongation nor contraction. At a certain distribution of building units over the various hierarchic levels—as roughly corresponding to a characteristic ratio of surface to volume—the system is found in a state of optimal hierarchic order (OHO). In passing this state (due to an increase in surface to volume ratio) the system appears to undergo transition into a "meltlike" state. It is proposed that the slope of the curve at the point of inflexion (and intersection) in the plot of load vs. rate of expansion or contraction may serve as a measure of the hierarchic order of the system under consideration. The question is raised in what ways observable changes in structure sensitive properties, such as strength or conductivity, may be related to changes in hierarchic order.

(Keywords: Extremely thin films; Structure-sensitive properties; Meltlike state; Phase transitions; Static and dynamic aspects of order)

Die hierarchische Ordnung im festen Zustand, 4. Mitt.: Zustände ,,optimaler hierarchischer Ordnung". Fest — ,,schmelzartige" Übergänge

Es wird versucht, die ,,ungewöhnlichen" Eigenschaften extrem dünner Filme und außerordentlich kleiner Kristalle verstehen zu lernen. Dabei wird vom bekannten Verhalten von Goldlamellen ausgegangen, welche beim Erwärmen schon weit unterhalb des Schmelzpunktes zusammenfließen. Unabhängig von der Temperatur gibt es für Filme gegebener Dicke und Vorbehandlung eine bestimmte Zuglast, unter der weder Schrumpfung noch Ausdehnung erfolgt. Es wird vorgeschlagen, daß das System bei einer bestimmten Verteilung der Bausteine auf die hierarchischen Ebenen, wie sie annähernd

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durch ein charakteristisches Verhältnis von Oberfläche zu Volumen gegeben erscheint, einen Zustand optimaler hierarchischer Ordnung (OHO) erreicht bzw. durchläuft. Beim Durchlaufen dieses Zustandes (infolge Erhöhung des Verhältnisses von Oberfläche zu Volumen) scheint das System in einen „schmelzartigen“ Zustand überzugehen. Es wird weiters vorgeschlagen, daß die Steigung am Wendepunkt der Kurven im Diagramm, in dem die Belastung gegenüber der beobachteten Kontraktion oder Expansion des Filmes aufgetragen ist, ein Maß der hierarchischen Ordnung des Systems darstellt. Schließlich wird die Frage gestellt, in welcher Weise beobachtbare Veränderungen von sogenannten strukturempfindlichen Eigenschaften — wie Festigkeit oder Leitfähigkeit — auf Veränderungen der hierarchischen Ordnung beruhen.

Introduction

Smekal[2] has pointed out that certain macroscopic properties of a solid material are more sensitive toward changes of its so-called "defect"-structure than others. Although he may have realized that full insensitivity is not possible, he proposed to distinguish between "structure-insensitive" and "structure-sensitive" properties. Examples for the former are lattice structure, lattice parameters, density and thermal expansion, and for the latter surface properties, hardness, strength, elasticity and chemical reactivity.

Although this concept has been found useful, no substantial further progress appears to have been made. The present authors ascribe this partly to the fact that *Smekal*'s formulation invited for questions about relations between properties and "defects" rather than "ordered relationships" within the system under consideration. Such questions suggest themselves according to the concept of the hierarchic order[1,3,4], which requires differentiation and ordered motions according to changing subordinations of the parts within any real system[1,3,4].

In order to gain an understanding of these features, questions must be raised not only about the static aspects of order, but also about the dynamically ordered relationships, although these are not directly observable and must be indirectly inferred.

Results and Discussion

States of "Highest Dynamic Order"

It is well-known that in a single crystal the static aspects of order are well developed. In its "rigidity" the crystal resists to structural changes up to the point where the dynamic aspects of order are so highly developed that the prevailing static aspects of order cannot be maintained any longer. (It has been stated in the previous paper of this series that the static aspects of order are dynamically maintained[1].) The crystal undergoes melting, sublimation or a phase transition (in the widest sense of the word) in the solid state. It has been established that in the course of a phase transition or recrystallization a "state" is passed, in which the values for the specific heat and for the entropy change are increased[5] to an extent which indicates that the system is inherently dynamic. In this "state" the system properties are nearly independent from the static aspects of order, such as defect structure[1]. This state of the system has been described as that of highest dynamic order (HDO); in other words: the different "structures" are both "interrelated" to each other and separated from each other by a "barriere" of a "state" of highly developed dynamic aspects of order, which is confined to a narrow temperature range[1].

The well developing dynamic aspects of order within the transition range are reflected in unusually high chemical reactivities, and this is known as the "*Hedvall* effect"[6–10]. For example, the reactions of alkaline earth metal oxides with silver nitrate set in at the so-called transition temperature of the latter. Likewise, powder metallurgical reactions are particularly fast in the range of recrystallization[6,11].

At temperatures both above and below the transition range the dynamic aspects of order are lower, and hence properties which are highly influenced by the dynamic aspects of order may exhibit different temperature coefficients below and above the transition range. Such effects are sometimes described as "anomalies" or even as "curiosities", for example with regard to the changes in magnetic and spectral properties of the so-called spin cross-over complexes of different "history"[1,5]. The anomalies" are found more pronounced the greater the hierarchic order of the system under consideration[1].

Can the Properties of Extremely Thin Films of Gold Be Explained by the Occurrence of a Transition from the Solid into a "Meltlike" State?

"Unusual" properties of thin films of gold have been described by *Chapman* and *Porter*[12] as well as by *Tammann* and *Boehme*[13] long ago. They studied the actions of temperature and mechanical forces on the properties of extremely thin layers of gold mounted upon a glass. The gold leaves were found to expand on heating up to a certain temperature. Above a temperature far below the melting-point of gold, the leaves were found to undergo considerable contraction. The shrinking rate was found greater the thinner the film and the higher the temperature. The temperature at which neither expansion nor contraction took place was found lower the thinner the film, namely 500 °C for a film thickness of 0.65 μm and about 200 °C for a film thickness of about 0.2 μm. These temperatures refer to electrolytically prepared films. They were found considerably higher after mechanical treatment[13] (Fig. 1). The rate of shrinking was decreased as the sample

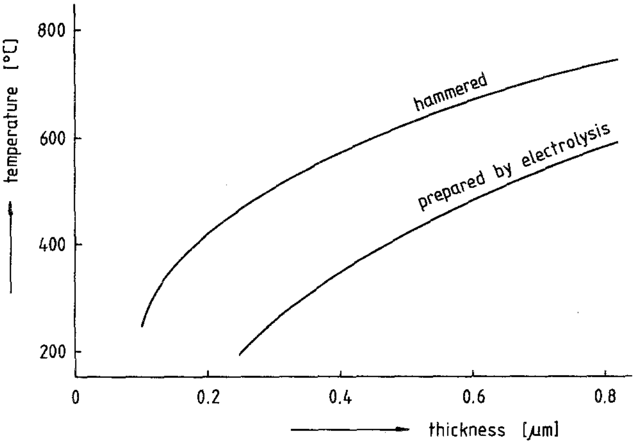

Fig. 1. The temperatures above which shrinking is observed for gold films of different thickness and different mode of preparation

was stretched. An electrolytically prepared sample of 0.65 μm thickness underwent neither elongation nor contraction, when it was subjected to a load of 2.4 g for a film 1 cm wide[13]. Under this load the said property was independent of temperature in the investigated range from 700 °C to 850 °C. Below the said rate the rate of contraction was greater, and above this load the rate of expansion greater the higher the temperature[13] (Fig. 2). The curves in the plot load vs. contraction and expansion respectively obtained for different temperatures show a point of intersection at a load of 2.4 g for a film 1 cm wide[13]. In this state the system has greatest ability to maintain its properties irrespective the temperature. This state depends on the thickness of the films. *Sawai* and *Nishida*[14] found this point for films of 0.77 μm thickness under a load of 1.5 g (Fig. 3). The system underwent neither contraction nor elongation over a wide range of load, when it was kept at a temperature around 650 °C (Fig. 3): at this temperature the system has a remarkable ability to maintain its properties under different loads.

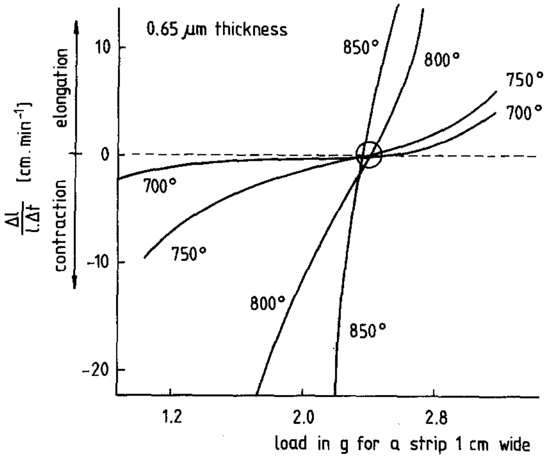

Fig. 2. Rates of contraction resp. elongation vs. strain for gold films of 0.65 μm thickness at temperatures above that of the state of OHO

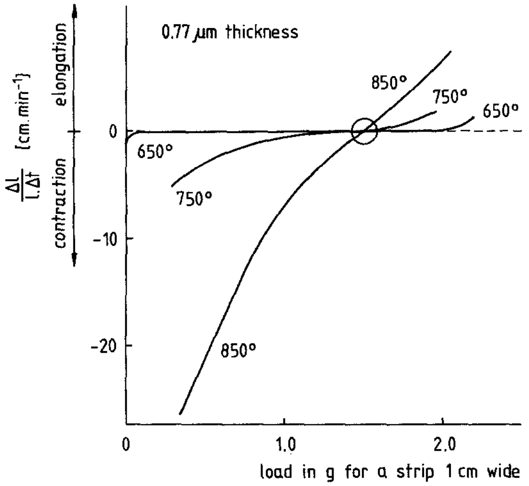

Fig. 3. Rates of contraction and elongation, respectively vs. strain for gold films of 0.77 μm thickness at temperatures above that of the state of OHO

Under load the contraction and expansion respectively is at 800 °C smaller the greater the thickness: in the load vs. contraction plot the curves obtained for different thickness give a point of intersection at a load of about 1.5 g for a film 1 cm wide (Fig. 4).

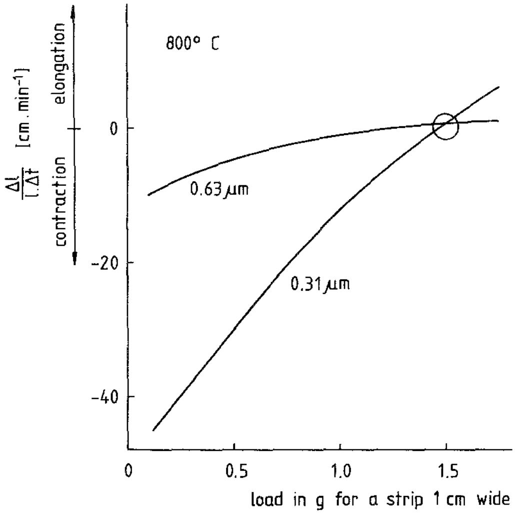

Fig. 4. Rates of contraction resp. elongation vs. strain for gold films of different thickness at 800 °C

All of the said properties resemble those which are found in the course of phase transitions. No phase transitions are observed in crystalline gold, but the changes in macroscopic properties in the course of passing the singular point suggest the formation of a *"meltlike" state*, and hence a *transition* from the crystalline state to a "meltlike" state. In extremely thin films and extremely small grains the defect structures are so highly developed that the properties of the pure crystals may be nearly lost. In other words, the samples under consideration are rather amorphous than crystalline; they have no longer a sharp melting-point, but rather a "softening"-range, as it is well known for the glassy state. The smaller the film thickness, the lower is the temperature at which such properties become developed. We may consider the singular point where neither expansion nor contraction occurs, as *"transition point"* between "solid" gold and "meltlike" gold, and the transition a *solid—"meltlike" transition.*

Does the Solid—"Meltlike" Transition Point Represent a State of Optimal Hierarchic Order (OHO)?

The said transitions are found for extremely thin films and for extremely small grains. At the solid—"meltlike" transition point the system has optimal ability to "defend" its properties toward changing environmental conditions, and this requires well developed dynamic relationships between all of the parts within the system. The properties at the solid—"meltlike" transition point differ, however, from the point of highest dynamic order (HDO), as it is passed in the course of a transition in the solid state[1] (from one crystalline phase into another crystalline phase). In the former the system reaches a state where the static aspects of order are still partly maintained. In the latter a transition state is passed in which the static aspects of order appear of little significance.

It appears to the authors that in a solid material the execution of the hierarchic order provides for the dynamic maintenance of the static aspects of order, i.e. its crystal structure[1]. This requires an "appropriate" number of building units in the lowest hierarchic level, i.e. a number of "normal" building units which is considerably greater than that in the higher hierarchic levels. This may be roughly expressed by a certain (small) ratio of surface to volume.

This condition is fulfilled in crystals of "reasonable" size. As the crystal size or the film thickness is decreased, the ratio of building units in the higher levels to those in the lowest level and the ratio of surface to volume is increased. A state will be reached in which the dynamic aspects of order are highly developed, and the static aspects of order, as characterized for the solid state, are still fully maintained. As the dynamic aspects of order are further increased, for example by increasing the temperature, by the actions of mechanical forces, or (and) by decreasing the film thickness or the grain size, the static aspects of order can no longer be maintained fully, as the number of building units in the lowest level has become too small to provide the *necessary framework in support for the static aspects of order*. The latter are, however, only partly lost, and the system has meltlike and solidlike properties at the same time. The system may restore the partial loss in its static aspects of order, in that the surface area is decreased, (the number of building units in the higher levels is decreased, and that in the lowest level is increased). In this way the system may approach a state in which the static aspects of order are more fully maintained. This state is reached fully at the singular point under consideration, in which the *dynamic aspects of order are highly developed in well-balanced relations to the static aspects of order*. The system has optimal flexibility toward the environment and optimal ability to conserve dynamically its static aspects of order. The authors propose that the system is in a *state of optimal hierarchic order (OHO)*. This state of OHO is established at a lower temperature the higher the ratio of surface to volume, i.e. the thinner the film or the smaller the grain size. The authors expect that the state of OHO is established under conditions of the so-called "milling equilibrium". Because the state of OHO depends strongly on the environmental conditions, the milling equilibrium can be defined only with respect to the environmental conditions, including the special milling conditions.

The decisive role of environmental conditions for the hierarchic order of a real solid is also shown by the great influence of the gas atmosphere on the shrinking of silver[15,16]. Most adsorption equilibria are known to show a negative temperature coefficient. This may be due to a more pronounced lowering of the dynamic aspects of order in the solid phase as the temperature is decreased than in the gas phase[17]. The enormous dependence of the properties of deposited films on the nature of the substrate and the modes of deposition and annealing procedures[18,19] is another example for the role of the environment. Its great influence on the hierarchic order of a solid phase is one of the reasons why in the illustration of the hierarchically arranged levels for the solid phase[3,17] the upper part of the pyramid has been omitted.

From the presented point of view many known phenomena may be seen in a new light. For example, the formation of small droplets of silver at 100 °C in the course of the reduction of silver oxide by hydrogen as found by *Szabó* and *Konkoly-Thege*[20]. This phenomenon suggests that the size of silver grains produced on the silver oxide surface is so small (the ratio of surface to volume so great) that they are in the "meltlike" state at a temperature as low as 100 °C. (It has been pointed out above, that gold films of 0.2 μm thickness reach this state at about 200 °C)! The rate of agglomeration of the grains (like the shrinking rate of a thin film) is rather high under these conditions. The small grains are readily transferred from the points of crystallization probably toward the centres of highest energy, i.e. the so-called craters, hitherto considered as three-dimensional defects[4], where the grains may flow into each other even at 100 °C!

Likewise, in the course of vapour deposition the formation of droplike islands of tin has been found to occur on a sodium chloride substrate[21]. Nuclei deposited on other areas are "captured" by the islands. As islands increase their size, the larger ones appear to grow by coalescence of the smaller ones, the disappearance of the latter being quite rapid (in less than a fraction of a second). The formation of larger islands is termed "increasing agglomeration", and this is increased as the rate of deposition is decreased[18,19,22,23]. This would not be expected on statistical grounds[19]. It is, however, in agreement with the presented view. Decrease in rate of deposition favours extremely small crystals in the meltlike state, and this means that their rate of agglomeration is great. The decisive role of the supporting material for exchange of information between adsorbed particles which seem "separated" from each other on the surface, is evidenced by the phenomenon of "co-adsorption"[24].

Solid—"meltlike" transitions may also provide an interpretation for the phenomena which have been observed in the so-called rheocast-process[25–27], and this will be treated in more detail in a subsequent paper. Solid—"meltlike" transitions also seem to be involved in the process of mechanical alloying[28], which consists of blending elemental powders with master alloy powders in an attritor and ball-milling these powders under a dry protective atmosphere. Cold-working and consolidation by extrusion yields a dense material, in which number and size of pores are higher than in the normally solidified alloy[29]. States of OHO may be approached or reached in many other systems, such as in colloids, aerosols, in the course of the production of ceramics and cement, powder metallurgy, dispersion hardening or mechanochemistry.

At a state of OHO the dynamic properties of the system are optimally developed in balanced relations to the static aspects of order, as they are characteristic for the solid under consideration. The situation is, however, different for a state of HDO, as it is passed in the course of a phase transformation or recrystallization in the solid state[1]: the dynamic aspects of order are developed to an extent that the original static aspects of order—as they are required for the solid state—are nearly lost. These differences lead the authors to distinguish between these states of highly developed dynamic properties, namely as states of OHO and HDO respectively.

In order to characterize the hierarchic order of a given system, it has been proposed to consider the slopes of the transition curves at the point of HDO for low spin—high spin transitions. Likewise, the state of OHO appears a suitable state of reference for the characterization of the hierarchic order. At a point of OHO the slope of the curve (in Figs. 2, 3 and 4) may be considered to express the hierarchic order of the system under consideration: the hierarchic order is greater the smaller the slope at the point of intersection of the curves denoting the solid—"meltlike" transition.

Relations Between Changes in Structure-Sensitive Properties and Changes in the Hierarchic Order?

The authors realize that the unfamiliar views presented in this and in the preceeding papers[1,3,4] may appear unnecessary from the point of view of the familiar models. They consider the usefulness of the new approach, in that it may help to raise new questions. For example, the question may be put forward, in as far there are relationships between changes in structure-sensitive properties and changes in the hierarchic order of the system under consideration. Examples for such questions are the following: Is the strength of a solid dynamically maintained, and in what ways is it related to the dynamic and static aspects of order? Is the surface tension independent from the surface to volume ratio, and are there remarkable changes in surface tension and in surface energy at the point of OHO? Do metal films exhibit a minimum electric conductivity at the state of OHO, and does the conductivity of an ionic conductor or of a semiconductor show a maximum at this state? In what ways is the state of OHO influenced by the history of the material, or by the actions of pressure, of irradiation or of fields?

In order to learn about such relations between changes in the hierarchic order and various observable properties, it would be desirable to know a great number of properties of the given real system under consideration (of given history) and their changes by given changes in environmental conditions. So far, experiments have been carried out on samples of different and usually unknown or not sufficiently specified history and even of unknown amounts of impurities. No results are known to the present authors which refer to changes in a number of physicochemical properties for the *same* sample subjected to the *same* change in conditions. It is realized that this may not be an easy task, but it appears desirable, in order to learn about the relationships between changes in macroscopic properties and changes in the hierarchic organization. Another difficulty is the fact that the mechanical properties show relations between the forces applied and a certain deformation of the material produced by them. Thus, materials of different mechanical properties are subjected to different forces during measurement. Finally, we may not be aware of the nature of the actions imposed on a system as caused by various changes in environment, which have not been considered so far.

Final Remarks

The concept of hierarchic order has in common with thermodynamics that it is based on experience and not on *a priori* propositions or on model assumptions. The second law of thermodynamics is based on the experience that it is impossible to produce a *perpetuum mobile* (of the second kind), and this has been found in full accordance with all known facts and observations. Likewise, the concept of hierarchic order is the result of the rationalization of observations and facts. It may even be stated that it might be *impossible to find a system which is not hierarchically organized*[30].

The authors propose therefore to take real objects as starting points for the investigation and to perform on each system an anamnesis about its properties as far as possible. The investigation should also be lead by the nature of the object rather than by the propositions of the scientist. Answers obtained under these circumstances may lead to a better understanding of nature, rather than of the ideas of scientists, and, with respect to the solid state, to open up new pathways in materials science and technology.

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