

Hans-Rainer Trebin (Ed.)

Quasicrystals

Structure and Physical Properties



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Cover Picture

Single-grain icosahedral Zn-Mg-Dy quasicrystal of diameter 1cm grown in the shape of a pentagon dodecahedron. Courtesy of Dr. Michael Feuerbacher, Forschungszentrum Jülich.

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Preface

The quasicrystalline state is a third form of solid matter beside the crystalline and the amorphous. The atomic positions are ordered, but with rotational symmetries, e.g. five-, eight-, ten- or twelfefold, which are not found in standard crystals. These symmetries forbid a periodic structure and, instead, enforce quasiperiodicity.

The discovery of quasicrystals in 1984 initiated new fields of research. New ways for a structural description had to be applied, like quasiperiodic tilings of space, irrational cuts through higher-dimensional crystals, or overlapping clusters. A new, “phase-” degree of freedom was predicted, making itself evident in atomic flip motions and accompanying diffusion and deformation processes. From quasiperiodicity, new localization properties of electrons and phonons were derived.

After the growth of larger samples was mastered (similar to the centimeter-sized single-grain icosahedral Zn-Mg-Dy quasicrystal on the cover), one could start to check structure and atom dynamics with elastic and inelastic scattering methods. Transport measurements displayed surprising results: Extremely high electric resistivity in aluminum dominated alloys, rising with the degree of order and falling with temperature. Mechanical measurements showed brittleness and hardness at low temperatures, but ductility with extreme deformability at high temperatures. Other observations, for example low friction, corrosion and oxidation resistance, low wetting of surfaces, hydrogen storage, strength of quasicrystalline-crystalline composites, promised technological applications. Quasicrystals became a prominent example for systems whose properties are strongly determined by their structure. The list of interesting problems increased.

Therefore in 1997, the Deutsche Forschungsgemeinschaft, Germany’s national science foundation, concentrated the quasicrystal research activities by establishing a Priority Programme “Quasicrystals: Structure and Physical Properties” (SPQK: Schwerpunktprogramm Quasikristalle). About 30 research groups from all over Germany proposed projects and applied for funds. The projects were panel reviewed during colloquia at Chemnitz (1997), Seeheim-Jugenheim (1999) and Irsee (2001). From the beginning, the members of the reviewer group not only came from research institutes in Germany, but also from France, Switzerland and the Netherlands.

Close bonds were all the time existing with a similar programme in France, the Groupe-ment de Recherche: Concertation pour l’Investigation des Quasicristaux (GDR-CINQ). With the French groups common progress colloquia were held at Strasbourg (1998) and Jülich (2000), well attended also by other European scientists. The closing colloquium of SPQK will take place at Nancy (May 2003). The collaboration of the SPQK labs was advanced by about 15 topical workshops, with participation of many experts from abroad, by mutual

visits and by shared services, in particular by central allocation of thoroughly characterized samples for the experimentalists. Particularly fruitful has been “tandem” work in the Priority Programme: Two labs working with the same methods in a competitive and simultaneously complementing way, publishing their results either in one work or closely synchronized.

The results of the efforts are collected in this book. The articles span almost all aspects of quasicrystal research and resemble the state of the art at the end of the year 2002. The contributions are arranged according to the topical grouping of the projects: A – Synthesis, metallurgy and characterization, B – Structure and mathematical modelling, C – Electronic and magnetic properties, D – Thermal and dynamic properties, E – Mechanical properties, and F – Surfaces and thin films. Emphasis has been placed in each contribution on a broad introduction before the hard research facts are being presented. Thus the book should be of great value both for the non-specialist and the researchers in the field. Each article has been refereed.

Sincere thanks are expressed to the Deutsche Forschungsgemeinschaft for making possible this programme, in particular to Programme Director Dr. Klaus Wehrberger, Bonn, to the review panel headed by Prof. Dr. Albrecht Goldmann, Kassel, and especially to those members of the panel, who refereed the contributions to this volume. I am deeply indebted to Christoph Rudhart, who carefully collected, checked and style-edited the electronically submitted papers, supported by Christian Ulrich. Also, I want to acknowledge the excellent collaboration with Mrs. Vera Palmer and Mrs. Cornelia Wanka from Wiley-VCH who made a publication possible three months after the manuscript was submitted.

Last but not least I want to thank all the members of SPQK for the inspiring cooperation, the lively colloquia and the many outstanding results. I express my appreciation for the discipline and quality by which the contributions to this final report were delivered despite very tight deadlines.

Hans-Rainer Trebin

Stuttgart, January, 2003.

Since the discovery of quasicrystals, approximately twenty years ago, the field of quasicrystal research has experienced an enormous development. Many of the riddles of the beginning have been solved and new subfields have opened. One understands now many of their special properties. This has been possible because of the contributions of scientists from many disciplines. From the beginning the field has been multi-disciplinary, and this is still the case, what makes it so interesting. Mathematicians, theoretical and experimental physicists, crystallographers, chemists and material scientists have worked together to get a better understanding of this form of matter.

In Germany many of the required disciplines were, and are, present and several research groups were interested. Therefore, it was an excellent idea to combine these groups into a network. Due to the financial support by the Deutsche Forschungsgemeinschaft a special programme could be organized as Priority Programme “Quasicrystals”, and this has been very successful.

Synthesis and characterization could be done at Frankfurt, München, Marburg, Dortmund, Jülich and Stuttgart, theoretical modeling and mathematical studies at Greifswald, Tübingen, München, Magdeburg and Chemnitz, electronic structure studies were performed at Chemnitz, Magdeburg and Karlsruhe, dynamical properties at Duisburg, Stuttgart, Münster and Chemnitz, mechanical properties at Jülich, Dresden, Stuttgart and Braunschweig and surfaces were studied at Stuttgart, Jülich, Berlin and Dortmund. Groups in almost twenty cities were involved. The studies by this network gave a broad coverage of the field of quasicrystals, and the results are very interesting. Therefore, I think it was a good idea to collect the main results in a scientific monograph, besides the required organizational reports.

The results of the cooperation, as they are presented in this book, range from basic experimental and theoretical ingredients to very practical knowledge. Very important in such a collaboration is the growth of samples. High-quality samples of the well known Al-Mn-Pd could be provided; also Zr based compounds and samples with other symmetries could be produced. The mathematical background was provided by studies of tilings and coverings, by a fundamental study of diffraction from quasicrystal compounds and by modeling of surfaces. Vibrational properties were investigated experimentally with neutron scattering techniques, and theoretically by model calculations. Studies of electronic properties range from model calculations to calculations with realistic potentials. Interesting results were obtained about diffusion and the atomic dynamics. On the other side of the range are the technological studies of mechanical properties, plasticity and the role of defects. Important, both from the fundamental and the applied point of view are studies of the structure and properties of quasicrystal surfaces. This broad range of topics touches upon all the important issues in the quasicrystal research. The results reported here are representative for the status of the field.

During the six years of its existence the German network was very active, what can be seen not only from the number of (joint) publications, but also from the number of workshops on various topics, and the attendance of the network meetings. That the network functioned so well was certainly also due to its coordinator, Professor Trebin, who did an excellent job. We can congratulate him, and all the members of the network for the achieved results.

Ted Janssen

Nijmegen, January, 2003.

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1 Synthesis, metallurgy and characterization

1.1 Single-quasicrystal growth

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1.1.1 Introduction

Since the discovery of quasicrystals in the early 1980's intense research has been focused on the central question if and how the physical properties of quasicrystals derive from their salient structural features. The decisive point for the success of experimental approaches addressing this question is the availability of high-quality samples, allowing for direct conclusions on the intrinsic physical properties without having to take into account additional, non-structure related influences, such as secondary-phase or grain-boundary effects. The development of a single-quasicrystal growth procedures is therefore an essential ingredient for the understanding of the physics of this new class of solid matter.

An important step towards the production of high-quality samples was the discovery of the first stable quasicrystals such as icosahedral Al-Cu-Fe [1], decagonal Al-Ni-Co [2] and icosahedral Al-Pd-Mn [3]. The latter phase was the first so-called "perfect" quasicrystalline material [4] for which a successful single-crystal growth procedure was reported [5]. Today, some hundred quasicrystalline phases are known, some tens of which are stable and therewith candidates for single-quasicrystal growth approaches.

Some facts make the development of a single-crystal growth procedure for these materials a technical challenge. Firstly, quasicrystals exclusively exist in complex intermetallic alloy systems, frequently possessing narrow stability ranges and numerous competing phases in close compositional vicinity. Besides the exception of the recently discovered Cd-based quasicrystals [6], all stable quasicrystals exist in ternary, i.e. three-component alloy systems, and are peritectic phases, i.e. they do not solidify congruently. Moreover, many quasicrystalline phases involve technically inconvenient elements such as Zn or Mg, which possess high vapour pressures impeding the applicability of elementary growth procedures. Hence, a successful production of these materials requires the development and application of highly advanced growth techniques. It should be pointed out that the same considerations hold for many crystalline intermetallic alloys – even for simpler binary crystalline phases very few successful single-crystal growth procedures have been established.

In this chapter we will describe single-crystal growth procedures developed for a number of quasicrystals and a related crystalline intermetallic alloy, a so-called approximant phase. We present a brief review of the thermodynamic fundamentals of crystal growth introducing the important terms of phase diagrams and solidification processes. We describe the three main growth techniques applied and finally present the technical details and the results of single-crystal growth procedures.

1.1.2 Solidification and phase diagrams of intermetallic alloy systems

Stable Quasicrystals and approximants exist to a broad majority in ternary alloy systems. As a prerequisite for the description of single-crystal growth procedures for these materials we therefore have to consider the phase diagrams of ternary alloy systems.

Let us firstly define some of the terms that will frequently be used throughout this chapter. An alloy is a (usually metallic) substance of two or more elements as either a compound or a solution. A system or alloy system comprises the totality of all possible alloys of a given set of elements. A phase is a portion of the system whose properties and composition are homogeneous and which is physically different from other parts of the system. The components of a system are the different elements making up the system, and their relative amounts give the composition of a phase. Phase transformations are changes from one or more phases to a new phase or a mixture of phases that can occur in a given system upon changing the composition and/or the outer conditions the system is subjected to, e.g. temperature or pressure. The reason why such changes occur is that under the given conditions the initial state of the alloy is unstable relative to the final state. The description (and definition) of stability and the relations to the outer conditions is provided by thermodynamics, saying that, if a system transforms at constant temperature and pressure, its relative stability is determined by its Gibbs free energy G . A system will be in equilibrium, i.e. in its most stable state where no changes occur ad infinitum, when it has the lowest possible value of G . A phase diagram, finally, is a multi-dimensional map of the equilibrium states of a system as a function of the composition and other outer conditions. Considering the growth of crystals one usually has to regard only the temperature as an outer parameter. Then the phase diagram of a two component alloy, i.e. a binary system, can be represented by a two-dimensional plot, the abscissa giving the composition and the ordinate giving the temperature. The phase diagram of a three-component system, i.e. a ternary alloy, can be represented as a three-dimensional object. The composition is indicated on an equilateral triangle whose corners represent 100 % of each element and the third axis, perpendicular to the triangle plane, is the temperature axis. Two-dimensional representations can be given as cuts perpendicular (isothermal sections) or parallel (isopleths or vertical sections) to the temperature axis. Let us visualize these terms considering a phase diagram possessing some features typical for intermetallic alloy systems. Fig. 1 shows a scheme of a binary or pseudo-binary phase diagram of the alloy system of the components A and B. The left and right edges of the diagram represent 100 % of component A and B, respectively. The vertical axis represents the temperature. T_A and T_B , therefore, are the melting temperatures of the pure components A and B respectively. The system contains four phases, α , β , γ , and the liquid phase L. Above the temperature T_A , only the liquid phase L exists. Furthermore we find five phase fields of mixtures of two phases, namely of α , β and γ plus liquid, of $\alpha + \beta$ and $\beta + \gamma$. The full lines separate the phase fields, and hence the phase diagram can be read such, that it tells us at which temperature which phase is in stable equilibrium for a given composition. Within the two-phase fields, the two respective phases coexist, that is we find two phases which are both in equilibrium in each others presence. For example, in the field L + β the β -phase is in equilibrium with the liquid and in the field $\beta + \gamma$ the β -phase is in equilibrium with the γ -phase. The α -phase field extends from the left edge of the diagram into a region containing some proportion of B. This means that the phase containing the element A exclusively, existing exactly on the left edge of the diagram, is capable to accommodate a small

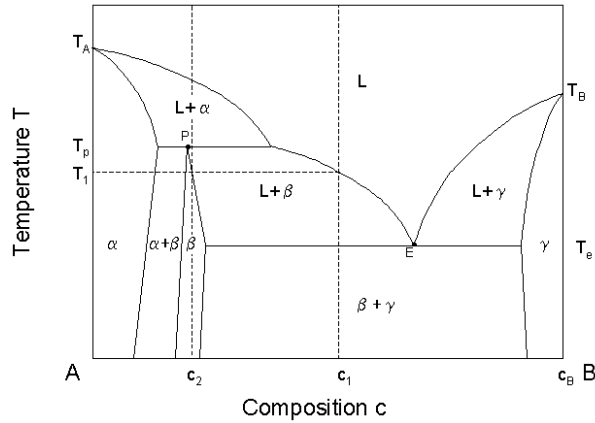


Figure 1: Scheme of a binary phase diagram (see text).

amount of element B. We then say that in this range of compositions B is soluble in α . Let us note, that the lines separating the liquid-solid two-phase fields from the liquid are termed liquidus lines, whereas those lines separating the liquid-solid fields from the corresponding solid phase field are termed solidus lines. For ternary alloys we correspondingly refer to these separations as liquidus and solidus surface, respectively.

The phase diagram is an indispensable tool to understand the solidification behaviour of a melt of given composition. For a simple case, consider a melt, i.e. a portion of material in the liquid state, of composition c_B . The location of this phase within the diagram is on the right edge above the temperature T_B . Lowering the temperature, as we would do in a solidification experiment, means that we follow the right edge of the diagram downwards, i.e. towards lower temperatures. As soon as we reach T_B , the material will solidify, i.e. a phase transition consisting of a change of L to γ will occur. The composition of the solid material is equal to that of the liquid phase. In this case we speak of congruent solidification, or, for the opposite case of heating the material, congruent melting. Now consider a melt of composition c_1 . The location of this phase within the diagram is on the dashed line of constant composition c_1 above the temperature T_1 . If we now decrease the temperature, i.e. we follow the dashed line of constant composition c_1 towards lower temperatures, a phase transition occurs when we meet the liquidus line at T_1 . Since we are entering the phase field $L + \beta$, the β -phase will get into equilibrium with the liquid, or, in other words, the phase which solidifies due to this treatment is β . Note that the β -phase has the composition c_2 , differing from that of the initial melt. In this case we speak of incongruent solidification (or incongruent melting). If we, on the other hand, cool down a melt with composition c_2 , solidification will not start with the β -phase but with the α -phase, since the first solid-liquid phase field we enter is $L + \alpha$. To put it the other way, if we wish to grow a crystal of the β -phase, we must choose the composition of the melt such that the first phase field entered is $L + \beta$. For this reason, a two-phase field $L + \xi$, where ξ stands for an arbitrary solid phase, is termed the primary solidification area for ξ .

The composition of the solidifying phase ξ lies on the solidus line of the phase field $L + \xi$. Upon further cooling, due to the slow diffusion processes in the solid phase, the composition