

# SYMPOSIUM K

## Quasicrystals

November 27 – 30, 2000

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\* Invited paper

## SESSION K1: METALLURGY, CRYSTAL GROWTH

Chair: Reinhard V. Lueck  
Monday Morning, November 27, 2000  
Room 203 (Hynes)

### 8:30 AM \*K1.1

GROWTH OF LARGE SINGLE-GRAIN QUASICRYSTALS FROM HIGH-TEMPERATURE METALLIC SOLUTIONS. I.R. Fisher, M.J. Kramer, A. Kracher, C. Song, A.I. Goldman and P.C. Canfield, Ames Laboratory, Iowa State University, Ames, IA.

The flux-growth technique has been successfully applied to several different families of icosahedral and decagonal quasicrystals and approximants, resulting in single-grain samples with volumes of up to (and in some cases over) a cubic centimetre. The technique clearly reveals the growth habit, and results in remarkably strain-free samples. Here, we describe the growth technique and present results of the sample characterisation.

### 9:00 AM K1.2

FORMATION OF QUASICRYSTALLINE PHASES IN THE EQUILIBRIUM IMMISCIBLE Co-Cu AND Fe-Cu SYSTEMS BY ION MIXING/SOLID-STATE REACTION. Z.F. Li, W.S. Lai, G.W. Yang, Q. Zhang and B.X. Liu, Tsinghua Univ, Dept of Materials Science and Engineering, Beijing, CHINA.

Anomalous structural evolution was induced in the Co-Cu and Fe-Cu multilayers by 100 or 200 keV xenon ion irradiation at 77 K or room temperature and some new metastable quasicrystalline phases were formed in these equilibrium immiscible systems. Nanosized quasicrystals were formed in an amorphous matrix, through a two-step transition of crystal-to-amorphous-to-quasicrystal, in the  $\text{Co}_{15}\text{Cu}_{85}$  and  $\text{Fe}_{70}\text{Cu}_{30}$  multilayered films. The obtained quasicrystals in the Co-Cu and Fe-Cu systems are dodecahedral and icosahedral phases with twelve-fold and five-fold rotational symmetries, respectively. The real compositions of the amorphous matrix were determined to be close to  $\text{Co}_{10}\text{Cu}_{90}$  and  $\text{Fe}_{70}\text{Cu}_{30}$ , while those for quasicrystals are nearly  $\text{Co}_{20}\text{Cu}_{80}$  and  $\text{Fe}_{50}\text{Cu}_{50}$ , respectively. Moreover, the same dodecahedral and icosahedral phases can also be obtained in the specifically designed  $\text{Co}_{50}\text{Cu}_{50}$  and  $\text{Fe}_{50}\text{Cu}_{50}$  multilayered samples upon thermal annealing at 500°C and 850°C, respectively, confirming the existence of these new metastable quasicrystalline states [1,2]. Concerning the uniformity of the formed phases, our molecular dynamics study showed that either Co or Fe could be mixed with Cu at an atomic scale to form some metastable alloy phases. Besides, the amorphous-to-quasicrystal transition was discussed in terms of the similarity in the atomic configuration between the icosahedral and amorphous short-range orders.

References:

1. G.W. Yang, W.S. Lai, C. Lin and B.X. Liu, Appl. Phys. Lett., 74, 3305 (1999).
2. Z.F. Li, Q. Zhang, D.P. Yu, C. Lin and B.X. Liu, submitted to Phys. Rev. B.

### 9:15 AM K1.3

PHASE DIAGRAM AND ELECTROSTATIC LEVITATION UNDERCOOLING STUDIES OF POLYTETRAHEDRAL PHASES IN Ti-Fe-Si-O AND Ti-Zr-Ni ALLOYS. T.K. Croat, J. Davis, A.K. Gangopadhyay, K.F. Kelton, G.W. Lee, J. Simmons, Dept. of Physics, Washington University, St. Louis, MO; Robert W. Hyres, Michael B. Robinson, Jan Rogers, Larry Savage, NASA/George C. Marshall Flight Center, Huntsville, AL; Thomas J. Rathz, University of Alabama, Huntsville, AL.

Ti/Zr-based quasicrystals are important for fundamental and practical reasons. They are replete with polytetrahedral phases, including icosahedral quasicrystals, high-order Fibonacci crystal approximants, and Laves phases. Ti-(Cr,Mn,Fe)-Si alloys require prodigious amounts of oxygen, between 6 and 20 at.%, to form the quasicrystal and crystal approximant; this is true of no other quasicrystal. The TiZrNi icosahedral phase is stable, forming by a solid-state transformation at low temperatures, rather than from the liquid as is true for all other stable quasicrystals, raising the possibility of a zero-temperature quasicrystal. Further, the quasicrystals and approximants may have important uses in structural and hydrogen storage applications. An improved understanding of the phase diagrams for these alloys is required to address the fundamental issues mentioned, to prepare better ordered samples for structural studies, and to develop processing routes for technological samples. Here, we present new phase diagram information for Ti-Fe-Si-O and Ti-Zr-Ni alloys near the quasicrystal and crystal approximant compositions.  $\alpha(\text{TiFeSiO})$ , the 1/1 crystal approximant, is shown to form peritectically from the liquid, indicating the possibility to produce single-crystal samples. Very long duration annealing studies demonstrate unambiguously that the TiZrNi i-phase and 1/1 approximant form at low temperatures by a solid-state transformation; their phase field does not extend to the liquidus temperature. The first undercooling measurements of electrostatically-levitated droplets of these Ti/Zr alloys are presented.

These nucleation studies provide new information on the structural relations between polytetrahedral phases and the undercooled liquid, and on the phase transformation process. The reduced undercooling for the polytetrahedral phases in these alloys is less than for crystal phases of a similar composition, verifying a low interfacial energy between the polytetrahedral phase and the liquid. This work was partially supported by the NSF (DMR 97-05202) and NASA (NCC 8-85 and NGT 5-50030).

### 9:30 AM K1.4

GROWTH, STRUCTURE AND ULTRASONIC INVESTIGATION OF ICOSAHEDRAL Zn-Mg-Y QUASICRYSTALS. Roland Sterzel, George Bruls, Wolf Assmus, Physics Institute, J.W. Goethe Univ, Frankfurt am Main, GERMANY; Aris Kounis, Gerhard Miehle, Materials Science Dept, Univ of Technology, Darmstadt, GERMANY.

Large icosahedral single crystals can be grown from the melt in the Zn-Mg-Y(RE=Ho, Er, Dy, Gd, Tb) system by the top seeded solution method. It is shown how the composition of the crystals grown from the melt shifts during growth. The shift of the composition is connected with a transition from the face centered icosahedral to the simple icosahedral structure. The history of the growth in this system is extracted from the composition gradient in a Zn-Mg-Y single crystal measured by wavelength dispersive x-ray analysis. The growth is discussed with respect to structural investigations performed on the R-phase. The cubic R-phase in the Zn-Mg-Er system is an approximant for the quasicrystal with overlapping icosahedral clusters. No large icosahedral clusters can be expected within this approximant. Both the growth behaviour and the structure of the R-phase fit to the random tiling growth model suggested by Joseph and Elser. Furthermore ultrasonic measurements on icosahedral Zn-Mg-Y single crystals are presented. Absolute values of the longitudinal and the transverse sound velocities as well as their temperature dependence are determined. The measurements also show the high quality of the quasicrystals grown by the top seeded solution method.

### 9:45 AM K1.5

EFFECT OF GROWTH RATE ON POROSITY IN Al-Pd-Mn ICOSAHEDRAL QUASICRYSTALS. A.R. Ross, I.R. Fisher, T.A. Lograsso, and P.C. Canfield, Ames Laboratory, Iowa State University, Ames, IA.

Growth experiments have been carried out to characterize the occurrence and development of porosity in Bridgman and flux grown Al-Pd-Mn icosahedral quasicrystals. In Bridgman growth of single grains of Al-Pd-Mn, it has been observed that the level of porosity fluctuates along the length of the crystal, implying that the development of porosity is affected by the local growth conditions. Experiments were conducted to evaluate the influence of the rate of solidification of the occurrence of porosity. Alloys were solidified over a range of growth rates using the Bridgman configuration, and at different cooling rates using the flux growth method. Porosity levels were analyzed via optical image analysis. Increasing growth/cooling rates induced a corresponding increase in the percent of porosity in the resultant crystals.

## SESSION K2: METALLURGY

Chair: Thomas A. Lograsso  
Monday Morning, November 27, 2000  
Room 203 (Hynes)

### 10:15 AM K2.1

SYNTHESIS OF BULK QUASICRYSTALS BY SPARK PLASMA SINTERING. E. Fleury, J.H. Lee, K.B. Kim, G.S. Song and D.H. Kim, Yonsei University, Center for Non-Crystalline Materials, Dept of Metallurgical Engineering, Seoul, KOREA; W.T. Kim, Chongju University, Dept of Physics, Chongju, KOREA.

Stable quasicrystals can be prepared by several techniques including conventional casting and sintering of quasicrystalline powders. Recently, the spark plasma sintering (SPS) process has received much attention as a method of making easily and quickly bulk ingots. Although SPS is commonly used to produce dense metal and engineering ceramics, no reports treat the application of this technique to produce bulk quasicrystals. In SPS, microscopic electric discharges applied between particles under low pressure (20-30MPa) enables powder compaction to a high density under uniform heating at a relatively low temperature and short time. In this study, we made an attempt by the SPS method to obtain specimens either with icosahedral, 1/1 cubic approximant, or decagonal quasicrystalline structure.  $\text{Al}_{62.5}\text{Cu}_{25.5}\text{Fe}_{12}$ ,  $\text{Al}_{57}\text{Cu}_{17.75}\text{Fe}_{14.75}\text{Si}_{10.5}$ , and  $\text{Al}_{75}\text{Ni}_{11.5}\text{Co}_{10.5}\text{Si}_3$  gas-atomized powders were used to prepare almost pore-free cylindrical specimens. Examinations of the microstructure indicated that the short sintering time avoided

exaggerated grain growth and that the phase constituents remained identical to the starting powders. Investigations on the effects of process parameters have revealed that the temperature and time of sintering affected the microstructure, and that the room temperature mechanical properties can therefore be optimized. The Vickers microhardness and the fracture toughness of these three alloy systems were found to be larger than those obtained from as-cast and hot pressed samples, which could be attributed to the small-grained microstructures of the SPS quasicrystals.

#### 10:30 AM **K2.2**

TRANSFORMATIONS IN HYDROGENATED Zr-Cu-Ni-AL QUASICRYSTALS. Daniela Zander, Uwe Köster, Dept. of Chemical Engineering, University of Dortmund, GERMANY.

The high number of potential interstitial sites for hydrogen and the favourable hydrogen-metal chemistry make quasicrystalline alloys candidates for hydrogen storage applications. Zr- as well as Ti-based quasicrystals have been observed to store hydrogen up to a content close to the best crystalline materials [1,2]. The objective of this paper is to present our recent results on the effect of hydrogen on  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  quasicrystals and their transformation reactions. Hydrogen charging was performed electrochemically in a 2:1 glycerin-phosphoric acid electrolyte. The microstructure of Zr-Cu-Ni-Al quasicrystals was investigated by xray diffraction and TEM and the kinetics of transformations by DSC and TDA. Hydrogen was observed to exhibit a significant effect not only on the formation of Zr-based quasicrystals from the glassy precursor material, but also on the stability of the Zr-Cu-Ni-Al quasicrystals. The icosahedral phase in  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  has been shown to absorb hydrogen up to  $H/M = 1.6$  which leads to an increase of the quasilattice constant by about 8% and microstructural changes as indicated by the weakening of the contrast of the quasicrystals in TEM as well as a disappearance of the weak diffraction spots in the corresponding diffraction pattern. Only partial desorption of hydrogen was observed to occur prior to the decomposition of the quasicrystalline phase. Desorption at lower temperatures is hindered by the formation of thin  $ZrO_2$  layers. DSC reveals that at low hydrogen contents the decomposition of the icosahedral quasicrystals is shifted to lower temperatures; at high hydrogen contents the formation of  $ZrH_{2-x}$  was revealed. The micromechanism of transformations during hydrogenation as well as the decomposition during annealing of hydrogenated Zr-based quasicrystals will be discussed in detail. [1] A.M. Viano et al., Phys. Rev. B51 (1995), 12026 [2] B.I. Wehner et al., Mat. Sci. Eng. A226-228 (1997), 1008

#### 10:45 AM **K2.3**

ON THE CORROSION MECHANISMS OF Al-Cu-Fe QUASICRYSTALS. Angelika Rüdiger, Uwe Köster, Dept of Chemical Engineering, University of Dortmund, Dortmund, GERMANY.

For an application of quasicrystalline coatings due to their good wear resistance and exciting low coefficient of friction a high corrosion resistance is of utmost importance. Therefore, the mechanisms of dissolution and passivation of bulk polycrystalline icosahedral  $Al_{63}Cu_{25}Fe_{12}$  specimens during electrolytic corrosion in 0.1 N NaOH and 1 N  $H_2SO_4$  were studied in detail. It was found that in 1 N  $H_2SO_4$  selective dissolution of Al and Fe occurs at the open circuit potential, which leads to a porous layer of recrystallized fcc Cu; after anodic polarization the dissolution of the alloy is followed by redeposition of Cu and formation of  $Cu_2O$ . On the other hand, in 0.1 N NaOH selective dissolution of Al was observed and a nanocrystalline layer consisting of  $Cu_2O$  and FeOOH forms at the open circuit potential as well as during anodic polarization up to -150 mV<sub>SHE</sub>. At higher potentials Cu-ions dissolve into the electrolyte, which allows Al to build up a hydroxide layer. Presumably due to the losses in Al during polarization phase transformations of the quasicrystals (e.g. continuous transformation or precipitation) were observed by transmission electron microscopy. In order to clarify the influence of the quasicrystalline structure on the corrosion, open circuit potentials and current densities of the quasicrystalline and three ternary crystalline phases with different Al-content, but approximately constant ratio Cu:Fe of 2:1 are compared in alkaline solutions. The comparison shows lower current densities, but a less noble open circuit potential for the quasicrystals than expected from the trend over the Al-content; thus indicating an influence of the quasicrystalline structure.

#### 11:00 AM **K2.4**

PHASE EQUILIBRIA AT INTERNAL INTERFACES OF ICOSAHEDRAL Al-Mn-Pd. Reinhard Lück, Tilo Gödecke, Max-Planck-Institut für Metallforschung, Stuttgart, GERMANY; Conradin Beeli, Solid State Physics Laboratory, ETH Zurich, Zurich, SWITZERLAND.

Highly faceted microholes (voids) in icosahedral Al-Mn-Pd quasicrystals form during annealing at temperatures between 750 and

830°C via classical Ostwald ripening [1]. The specimens were single-phase icosahedral with a composition of  $Al_{71}Mn_9Pd_{20}$ . If such a specimen containing voids is cooled to room temperature with a constant cooling rate of typically 0.6 to 5 K/min, the facets of the voids are frequently found to be decorated by a different material. The decorations have typically a fractal-like morphology. Specimens rapidly quenched after isothermal heat treatments around 800°C never showed similar decorations.

By X-ray microanalysis in a scanning electron microscope it has been found that this decoration material is considerably poorer in Al-content than the icosahedral phase, namely:  $Al_{63.5}Mn_{11.5}Pd_{25}$ . This measured composition is, however, influenced by the presence of the underlying icosahedral matrix and thus the real composition of the decoration may be closer to approximately  $Al_{60}Mn_{10}Pd_{30}$ . Accordingly, these decorations are precipitations at the surfaces of voids inside a single-phase icosahedral matrix. This implies that these decorations are formed at the void surfaces by a diffusion induced local equilibrium. The local equilibrium can be understood on the basis of the equilibrium phase diagram despite of the fact that the overall equilibrium results in a single icosahedral phase.

[1] C. Beeli, T. Gödecke and R. Lück, Phil. Mag. Lett. **78**, 339 (1998).

#### 11:15 AM **K2.5**

SOLIDIFICATION AND MICROSTRUCTURE CONTROL OF Mg-RICH ALLOYS IN THE Mg-Zn-Y TERNARY SYSTEM. Eun Soo Park, Seunghoon Yi, Jae Bum Ok, Won Tae Kim, Do Hyang Kim, Yonsei Univ., Center for Noncrystalline Materials, Dept. of Metallurgical Eng., Seoul, KOREA.

Icosahedral phases (I-phases) that have quasiperiodic atomic structure have been reported in many alloy systems. I-phases have attractive mechanical/physical properties attributed to their unique atomic structure. For instances, high strength at elevated temperatures and low friction coefficients of the I-phase have been reported in the alloy system Al-Fe-Cu. However, monolithic I-phase materials have poor ductility inhibiting structural applications. One reasonable solution for the structural applications is fabricating composite materials comprising an I-phase and a ductile phase. For these composite materials design, thermally stable I-phase equilibrating with a metallic solid solution is needed. In the Mg-Zn-Y system, thermodynamically stable I-phase exists having the stoichiometry of about  $Mg_{42}Zn_{50}Y_8$ . In this study, we study the solidification behaviors and phase equilibria in the Mg-rich corner of the Mg-Zn-Y system. The existence of the (I-phase  $\alpha$ -Mg) two phase field in the alloy system Mg-Zn-Y provides an opportunity to develop structural composite materials. The microstructures including the I-phase and a ductile phase,  $\alpha$ -Mg solid solution, are explored for the development of in-situ composites. By controlling thermal processing procedures, various (I-phase  $\alpha$ -Mg) microstructures including a eutectic microstructure can be developed expanding the microstructural options available for the structural composite materials comprising the I-phase and  $\alpha$ -Mg solid solution.

#### 11:30 AM **K2.6**

ENHANCEMENT OF THE ICOSAHEDRAL QUASICRYSTALLINE PHASE FORMING ABILITY WITH Be ADDITION TO AN  $Al_{62}Cu_{25.5}Fe_{12.5}$  ALLOY. S.M. Lee, B.H. Kim, D.H. Kim, and W.T. Kim, Center for Noncrystalline Materials, Dept. of Metallurgical Eng., Yonsei Univ., Seoul, KOREA.

The quasicrystal forming ability, solidification structure, thermal stability, and phase relationships of a series of conventionally-cast  $Al_{62-x}Cu_{25.5}Fe_{12.5}Be_x$  ( $x=0, 1, 3, 5, 7$ ) alloys were investigated. Icosahedral quasicrystalline phase (I-phase) nucleates first and then grows in a dendritic manner and remaining liquid solidifies into the metastable  $\tau$  phase at later stage of solidification during conventional casting when  $x>3$ . Single icosahedral quasicrystalline phase was successfully obtained by partial replacement of Al with Be (7 at.%) in an  $Al_{62}Cu_{25.5}Fe_{12.5}$  alloy during crucible cooling. The I-phase forming ability is greatly improved since the liquid melt can be undercooled to L I-phase region under the condition of conventional casting when the Be content is high ( $x>3$ ). The kinetic barrier for transformation into single I-phase by heat treatment is also greatly reduced if the I-phase forms by a primary solidification reaction ( $x>3$ ) rather than by the peritectic reaction ( $x=0,1$ ). The I-phase in an  $Al_{55}Cu_{25.5}Fe_{12.5}Be_7$  alloy has the same face-centered icosahedral structure as that in an  $Al_{62}Cu_{25.5}Fe_{12.5}$  alloy, and is of high quality without phason strain. Hardness of the I-phase increases with  $x$ , i.e. from  $H_v$  710 for  $x=1$  to  $H_v$  809 for  $x=7$ . Keywords: Al-Cu-Fe alloy, effects of Be addition, single icosahedral quasicrystal, conventional casting, thermal stability, hardness.

#### 11:45 AM **K2.7**

STABLE ICOSAHEDRAL QUASICRYSTALS IN THE Cd-BASED ALLOYS. Junqing Guo, Eiji Abe, An-Pang Tsai, National Research Institute for Metals, Tsukuba, JAPAN.

Stable icosahedral phases have been found in the Cd-based alloys.

These icosahedral alloys have quasilattice parameters from 0.5571 to 0.5799 nm. Electron diffraction study confirmed that the icosahedral quasicrystals have a primitive icosahedral structure. Formation processes of the icosahedral quasicrystals will be discussed.

### SESSION K3: STRUCTURE - DIFFRACTION

Chair: Eiji Abe

Monday Afternoon, November 27, 2000

Room 203 (Hynes)

#### 1:30 PM \*K3.1

WHERE ARE THE ATOMS IN QUASICRYSTALS? AN EXPERIMENTAL AND THEORETICAL MODEL OF QUATERNARY APPROXIMANTS. Gordon J. Miller, Chi-Shen Lee, Wen-Juan Tsai, Department of Chemistry and Ames Laboratory/US-DOE, Iowa State University, Ames, IA.

Problems concerning complete structural characterization of quasicrystals involve locating the atomic positions and determining the distribution of elements at each site. Quasicrystalline approximants provide models for potential building units of quasicrystals, but a clear determination of the elemental arrangements in such approximants also remains incomplete. We report experimental and theoretical studies of new, quaternary Bergman phases in the Li-Mg-Zn-Al system and a new, quasicrystalline approximant  $\text{Li}_{10}\text{Mg}_6\text{Zn}_{31}\text{Al}_3$  ( $\text{A}_{16}\text{M}_{34}$ -type). A theoretical model using averaged Mulliken populations provides a means to track the segregation of elements (and vacancies) onto different sites as a function of valence electron concentration. As the Li content decreases, vacancies begin to occur at a specific site in the Bergman structure. The new approximant demonstrates how truncated tetrahedral can play an important role in forming clusters with possible fivefold symmetry in quasicrystalline structures. We apply the theoretical model to other approximants, e.g. Mackay-type structures, in main group and transition metal systems as well.

#### 2:00 PM \*K3.2

APPROXIMANTS - THE KEY FOR UNDERSTANDING QUASICRYSTAL STRUCTURES. Walter Steurer, Katja Lemster, Michael A. Estermann, Antonio Cervellino, Torsten Haibach, Laboratory of Crystallography, ETH Zurich, SWITZERLAND.

"Where are the atoms?" Even fifteen years after Per Bak posed this question at the very beginning of quasicrystal structure analysis the answer is not fully known. Fundamental questions such as "are quasicrystals perfectly ordered or only on average quasiperiodic" are still open. Crucial for the understanding of quasicrystal structures was the discovery and study of more and more approximants in the last decade. Approximants are observed in all binary and ternary intermetallic systems where also quasicrystals are found. They have periodic crystal structures built from the same structural units as quasicrystals. A rational approximant results formally from the same higher-dimensional crystal as the parent quasicrystal. A big advantage is that approximant structures can be solved with standard crystallographic methods. An overview will be given about the actual state of quasicrystal and approximant structure analysis.

#### 2:30 PM K3.3

STATISTICAL TILING ANALYSIS OF A HIGHLY PERFECT DECAGONAL Al-Co-Ni QUASICRYSTAL. C. Beeli, C. Soltmann, ETH Zurich, Solid State Physics Lab., Zurich, SWITZERLAND; S. Ritsch, Inst. for Materials Research, Tohoku University, Sendai, JAPAN.

High-resolution TEM images of highly perfect decagonal Al-Co-Ni quasicrystals are investigated by a new, automatic tiling analysis described in detail in our second contribution to this conference. Former geometric analysis of tilings which were constructed from HRTEM images of highly perfect Al-Co-Ni quasicrystals indicated that these patterns are very close to a perfect Penrose tiling [1]. New high-voltage high-resolution electron micrographs have been obtained from  $\text{Al}_{70.3}\text{Co}_{7.3}\text{Ni}_{22.4}$  (quenched from 1170 K) in order to analyse the tilings on the basis of a covering cluster model as proposed by Gummelt [2] as well as Jeong and Steinhardt [3]. Moreover, the image contrast of single clusters has been studied in detail: Most clusters are mirror symmetric only, as required by a Gummelt decoration, whereas a smaller fraction shows a 10-fold symmetric image contrast. Additionally, HRTEM image simulations based on different structure models are presented and compared to the HRTEM images. The tiling analysis reveals that different tilings can be superimposed onto the HRTEM images with tau-scaled edge lengths: 0.75 nm, 1.24 nm, 2.0 nm, 3.2 nm and 5.2 nm, indicating the presence of approximate inflation/deflation symmetry.

[1] S. Ritsch, et al., *Phil. Mag. Lett.* **74**, 99 (1996)

[2] P. Gummelt, *Geometriae Dedicata* **62**, 1 (1996)

[3] H.-C. Jeong, P.J. Steinhardt, *Phys. Rev.* **B55**, 3520 (1997)

#### 2:45 PM K3.4

CHEMICAL ORDERING IN  $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$  DECAGONAL QUASICRYSTALS. Yanfa Yan, National Renewable Energy Laboratory, Golden, CO; S.J. Pennycook, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN.

We present first-principles total energy calculations on structures pertinent to the  $\text{Al}_{72}\text{Ni}_{20}\text{Co}_8$  decagonal quasicrystals. We find that it is energetically favorable for chemical ordering between Al and transition metals to take place in the central ring of the 2 nm clusters. This results in broken symmetry that restricts the possible overlaps between neighboring 2 nm clusters and enforces the perfect quasiperiodic tiling. Implications for the stability of this phase are discussed.

### SESSION K4: STRUCTURE

Chair: Conradin M.H. Beeli

Monday Afternoon, November 27, 2000

Room 203 (Hynes)

#### 3:30 PM \*K4.1

STRUCTURE OF APPROXIMANTS. Michel Boudard, LTPCM/ENSEEG, CNRS/INPG/UJF, St Martin d'Heres, FRANCE.

The structure of two decagonal approximant phases showing the importance of chemical ordering are reviewed in the Al-Pd-Mn system. Based on these structures a general description for these and other related phases in term of pentagonal chains of transition metals is introduced. Finally the relation with structural models for decagonal quasicrystals based on approximants are discussed in relation with the hypothesis of a unique cluster building a quasiperiodic structure and considering the presence of pentagonal chains of transition metals in the periodic approximants.

#### 4:00 PM K4.2

CRYSTAL STRUCTURE OF NEW APPROXIMANT HEXAGONAL PHASE IN Al-Fe-V-Si SYSTEM. Vladimir Ezersky, Avi Rochman, Michael Talianker, Dept of Materials Engineering, Ben-Gurion University of the Negev, Beer-Sheva, ISRAEL.

A model is proposed for the atomic structure of the new hexagonal Al-Fe(V)-Si phase recently found in rapidly solidified Al-Fe(V)-Si alloys. Its structure is closely related to well known cubic approximant  $\alpha$ -(Al-Fe-Si) phase and can be described as hexagonal packing of double Mackay icosahedral units similar to those from which the  $\alpha$  phase is built up. In the hexagonal phase these icosahedral units interconnect along irrational  $[1\bar{7}0]$  direction ( $\tau \approx 1.618$ ) so that they are rotated with respect to each other by 60 deg. around their twofold axis. This is in contrast to the  $\alpha$  phase where all double Mackay icosahedra are oriented parallel one another. A unit cell of the hexagonal phase consists of 490 atoms; the complete list of the sites and atomic coordinates is presented. For the determination of atomic positions in the unit cell the methods of crystallographic processing of high-resolution images combined with computer simulation techniques were used. Although the refinement procedure was not accomplished because of the difficulties in creating an adequate three-dimensional data set of diffraction intensities, it is believed that the atomic coordinates proposed in this work are sufficiently accurate. A proposed model is in good agreement with the experimentally observed high resolution electron microscopic images and electron diffraction patterns. The experimentally observed alpha-to-hexagonal phase orientation relationships can be easily deduced from the model.

#### 4:15 PM K4.3

THE LOCAL ATOMIC STRUCTURE OF R-Mg-Zn, (R = Y, Gd, Dy and Tb). M.J. Kramer, P.C. Canfield, I.R. Fisher, Seung-Tae Hong, and A.I. Goldman, Ames Laboratory, Iowa State University, Ames, IA; Y. Zhu, Brookhaven National Laboratory, Upton, NY.

The rare earth element in the R-Mg-Zn system provides a unique probe of the atomic structure of a face-centered icosahedral (fci) quasicrystal (qc). Unlike many of the other ternary and higher component qc systems, the compound around  $\text{R}_8\text{Mg}_{42}\text{Zn}_{50}$  allows for the substitution of one of its main components (R = Y, Er, Ho, Dy and Tb) without any appreciable change in its qc structure (space group or quasi-unit cell dimension). The large atomic mass difference between Y and the heavy rare earth elements afford large differences in the scattering cross-sections for electrons, neutrons and x-rays. Using high quality flux grown single grains with resolution limited diffraction peaks, the local atomic structure was probed with a variety of complimentary techniques. The differences in the pair distribution function (PDF) due to loss of the anti-ferromagnetic ordering of the Tb between 4.2 and 30 K was used to probe the R site. High resolution TEM and XRD have been used to solve the local structure. Results of this work suggest that there are local clusters in

this fci compound consisting of 5 concentric polyhedra with 124 atoms: an icosahedron, dodecahedron, icosahedron, C-60 and a dodecahedron, similar to previous work.[1] However, the HRTEM results indicate that the local structure consists only of these 5 shells which may edge share with the next cluster. Based on this atomic arrangement, the PDF results are consistent with R atoms partially occupying the vertices of the outer icosahedron and dodecahedron. This work was performed at Ames Laboratory, and was supported by the Director of Energy Research, U.S. Department of Energy, under contract No. W-7405-ENG-82. 1. Ohno, T. and T. Ishimasa, Proc. 6th. International Conf. On Quasicrystals, World Sci. in; S. Takeuchi, T. Fujiwara (Eds.) (1998), 39.

#### 4:30 PM K4.4

SUPERLATTICES, MODULATED STRUCTURES, NANO-CRYSTALS AND QUASICRYSTALS IN Mg-Zn-Re ALLOYS. Anandh Subramaniam, S. Ranganathan, Department of Metallurgy, Indian Institute of Science, Bangalore, INDIA.

Alloys in the Mg-Zn-RE systems have given new insights into the structure of quasicrystals and their relation to crystals. Icosahedral and decagonal quasicrystals and hexagonal phases related to them have been reported in these systems. Using TEM we study the formation of a variety of structures in the Mg-Zn-Y and Mg-Zn-La systems. Formation of Icosahedral phase, F.C.C superlattices and nanocrystals are seen in the as-cast alloy with nominal composition of  $Mg_4Zn_9Y_2$ . Hexagonal superlattices and modulated structures are formed in the alloys with higher Y (10% and 25% Y respectively). A variety of superlattices are observed in the Mg-Zn-La alloys (La = 6% and 9%). Some of these phases display interesting streaking in the SAD patterns. These phases are analyzed keeping in view their relation to the quasicrystals of the Mg-Zn-RE systems.

#### 4:45 PM K4.5

CHARACTERIZATION OF Ga-Mn NANO-SIZED QUASI-CRYSTALLINE AND CRYSTALLINE PARTICLES IN GaAs BY PEELS COMBINED WITH Z-CONTRAST IMAGING. K. Sun, I.A. Rauf, N.D. Browning, Department of Physics, University of Illinois at Chicago, Chicago, IL.

Integration of quasicrystals and approximants with commercially important materials, such as semiconductors, may lead to many new applications. Ga-Mn nano-quasicrystalline and crystalline particles have been successfully grown epitaxially in GaAs compound semiconductors, which have been studied by high-resolution transmission electron microscopy (HRTEM). These materials are further characterized by atomic resolution parallel electron energy-loss spectroscopy (PEELS) combined with Z-contrast imaging in a scanning transmission electron microscope (STEM). Electronic and optical properties of such nano-sized Ga-Mn quasicrystals, approximants and normal crystals are derived from low energy loss PEELS measurements using the Kramers-Kronig (K-K) analysis. The PEELS obtained showed sharp white lines found at the onsets of the Mn  $L_2$  and  $L_3$  absorption edges. Manganese d-band occupancies in these Ga-Mn crystals with different structures are determined by probing the Mn  $L_2$  and  $L_3$  edges.

### SESSION K5: STRUCTURE - DEFECTS

Chair: Do Hyang Kim  
Tuesday Morning, November 28, 2000  
Room 203 (Hynes)

#### 8:30 AM K5.1

IMAGE PROCESSING AND STATISTICAL ANALYSIS OF HRTEM IMAGES OF DECAGONAL QUASICRYSTALS. C. Soltmann, C. Beeli, ETH Zurich, Solid State Physics Lab., Zurich, SWITZERLAND.

High-resolution TEM images of decagonal quasicrystals often show an image contrast from which a tiling can be derived in principle. So far, image interpretation and tiling analysis were done manually and were restricted to a few hundred tiling vertices. Image contrasts are rapidly varying due to thickness changes as well as defocus variations. Therefore, automatic tiling analysis including conventional pattern analysis algorithms like pattern matching or cross correlation did not provide satisfactory results. Our algorithm based on image transformation is considered to better overcome the most common difficulties and to reliably yield sufficiently large sets of vertices. We present the underlying algorithm and its actual implementation which can be used generally for all polygonal quasicrystals. The algorithm has been applied to different images of decagonal quasicrystals so far. Examples are given which include the initial image preparation by image transformation and tiling analysis. Since it is now possible to obtain sufficiently large sets of tiling vertices, meaningful statistical

analysis of the long-range order can be made, which may permit statements on the quality and the type of tiling of the quasicrystal under investigation. For example, the analysis based on the approach described by Joseph et al. [1] can be applied. What is more, our algorithm provides sets of tiling vertices which are not biased by the inspection of the HRTEM image by a human operator.

[1] D. Joseph, S. Ritsch and C. Beeli, Phys. Rev. B55, 8175-8183 (1997)

#### 8:45 AM K5.2

DIFFRACTION FEATURES AND HYDROGEN IN  $Ti_{41.5}Zr_{41.5}Ni_{17}$  QUASICRYSTALS. E.H. Majzoub, K.F. Kelton, Washington University, Department of Physics, St. Louis, MO.

Experimental and theoretical studies of the atomic structure of hydrogenated and unhydrogenated icosahedral (i-phase)  $Ti_{41.5}Zr_{41.5}Ni_{17}$  are reported. They provide more information about the i-phase structure than studies of only unhydrogenated samples. Neutron and x-ray powder diffraction data from i-phase samples, as well as structural information about the related crystalline Fibonacci 1/1 approximant, were used to construct a Bergman cluster based icosahedral glass model. Comparison of experimental data with simulated neutron and x-ray powder diffraction demonstrates that the Bergman cluster is a frequently occurring element in the structure. Cluster packing fractions in the glass model can be varied; those near 0.55 give the best agreement with the diffraction data. Adsorbed hydrogen is known to locate preferentially in tetrahedral interstitial sites in many metals. Therefore some tetrahedral sites in a second structural model, based on tilings of canonical cells, were filled with hydrogen. Quasicrystal samples can be loaded with hydrogen up to a hydrogen to metal atom ratio of 1.89, consistent with the maximum filling allowed in the tiling model, while still obeying the Switendick criterion. Powder neutron diffraction spectra calculated from the hydrogen-filled tiling model are shown to be strikingly similar to those obtained experimentally from the hydrogenated quasicrystal.

#### 9:00 AM K5.3

UNRAVELLING THE STRUCTURE OF DECAGONAL APPROXIMANTS BY "BRUTE FORCE" DECONVOLUTION OF THE EXPERIMENTAL AUTOCORRELATION FUNCTION. Michael A. Estermann, Walter Steurer, Laboratory of Crystallography, Swiss Federal Institute of Technology, Zurich, SWITZERLAND.

Methods for the ab initio structure analysis of approximant phases with large unit cells and strong pseudosymmetry are presented. An approximant is a three-dimensional periodic intermetallic compound which typically has a large unit cell and contains hundreds or thousands of atoms. Typically an approximant contains the same clusters and building blocks as the related quasicrystal. The diffraction pattern exhibits strong decagonal pseudosymmetry and contains a large number of weak Bragg reflections. As a consequence, the standard crystallographic methods for ab initio structure solution (direct methods) fail. Alternatively, the "brute-force" deconvolution of the experimentally measured autocorrelation function allows to unravel the approximant structure without prior knowledge about the structure-building clusters [Estermann, M.A. (1995) Nucl. Instr. Meth. Phys. Res. A, 354, 126]. Examples are presented for the systems Al-Co-Ni and Al-Co-Ta.

#### 9:15 AM \*K5.4

ANALYSIS OF MAGIC CLUSTERS MADE FROM LASER-VAPORIZED ICOSAHEDRAL Al-Pd-Mn. C.J. Jenks, J.A. Barrow, D.J. Sordelet, M.F. Besser and P.A. Thiel, Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA; E.F. Rexer and S.J. Riley, Chemistry Division, Argonne National Laboratory, Argonne, IL.

Laser vaporization of an icosahedral Al-Pd-Mn sample with detection by time-of-flight mass spectrometry is used to probe metal clusters made from the intermetallic. After sample vaporization, clusters form by gas aggregation and may contain from a few to hundreds of atoms. Multiphoton ionization/fragmentation of these clusters yields mass spectra showing some cluster sizes with enhanced intensity, implying a special stability for these "magic cluster" sizes. The mass spectra, both of the naturally occurring alloy and of an alloy containing isotopically purified Pd, are used to determine possible atomic compositions of the magic clusters. Reactions of the clusters with simple molecules are used to probe cluster geometrical structure. Electronic structures are investigated by variations in cluster photoionization efficiency near threshold. Results of these studies and their relation to proposed cluster structures in quasicrystalline materials will be presented. Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences under Contract No. W-405-Eng-82 (Ames) and the Division of Chemical Sciences under Contract No. W-31-109-Eng-38 (ANL).

### 9:45 AM K5.5

HIGH PRESSURE STUDIES OF QUASICRYSTALS. Anne Sadoc, LPMS, Université de Cergy-Pontoise, Cedex, FRANCE and LURE, Cedex, FRANCE; Jean-Paul Itié, Alain Polian, PMS, Université P. et M. Curie, Cedex, FRANCE and LURE, Cedex, FRANCE; Kenneth Kelton, Dept of Physics, Washington University, St. Louis, MO.

High pressure X-ray diffraction studies of quasicrystals in hydrostatic conditions have demonstrated the high stability of icosahedral quasicrystals. Moreover, they have allowed to obtain the evolution of the six-dimensional lattice parameter versus pressure and to measure the zero-pressure bulk modulus and its pressure derivative. However, these studies are rather difficult since drastic conditions are required to obtain reliable data 1-6. This behaviour appears specific to quasicrystals. We will show the difficulties encountered in doing such experiments in exemplifying them with the study of two quasicrystals, AlCuRu and TiNiZr, in order to point out this unusual and intriguing behaviour of quasicrystals. Some new results in the hydrogenated TiNiZr alloy will also be presented. 1- A. Sadoc et al., Phil. Mag. B, 70, 855 (1994). 2- S. Lefebvre et al., Phil. Mag. B, 72, 101 (1995). 3- A. Sadoc et al., Phil. Mag. A, 74, 629 (1996). 4 - A. Sadoc et al., Phil. Mag. A, 77,115 (1998). 5- A. Sadoc et al., Proceedings of the international conference on aperiodic crystals, ed. M. de Boissieu, J.L. Verger-Gaugry and R. Currat, World Scientific, 1999, p. 463. 6 - A. Sadoc, J.P. Itié, A. Polian, J.Y. Kim, K.F. Kelton, Proceedings of the 7 th international conference on quasicrystals, Stuttgart (20-24 septembre 1999), Materials Science and Engineering A, under press.

### SESSION K6: DEFECTS - DISLOCATIONS

Chair: Hans-Rainer Trebin

Tuesday Afternoon, November 28, 2000

Room 203 (Hynes)

### 10:30 AM \*K6.1

ATOMIC DEFECTS IN AlPdMn: A STUDY BY MEANS OF POSITRON ANNIHILATION SPECTROSCOPY AND TIME DIFFERENTIAL DILATOMETRY. F. Baier, H.-E. Schaefer, ITAP, Stuttgart University, Stuttgart, GERMANY.

Starting from the wealth of knowledge on atomic defect properties in intermetallic aluminides [1,2,3] substantial progress has been made in studying thermal atomic defects in icosahedral AlPdMn quasicrystals. The thermodynamics and kinetics of thermal vacancies in icosahedral Al<sub>70.2</sub>Pd<sub>21.3</sub>Mn<sub>8.5</sub> were studied specifically and sensitively by detailed positron annihilation experiments, as well as by time-differential high-resolution dilatometry.

One part of the study are the first in-situ measurements of the positron lifetime in the temperature range from room temperature up to the melting temperature  $T_m$  of the icosahedral AlPdMn quasicrystals. After very slow cooling, a reversible increase of the mean positron lifetime could be observed in contrast to earlier investigations performed by other groups.

It appears that vacancy formation occurs in an aluminum rich environment with a complex positron trapping processes and with a low mobility. This may have implications on the structural models of quasicrystals, diffusion processes, and mechanical properties.

In recent time-differential high-resolution dilatometry, studies after fast temperature changes, the time dependent length change due to the thermal defect formation was studied, additionally yielding defect kinetics similar to those observed in positron lifetime studies.

- [1] R. Würschum, C. Grupp and H.-E. Schaefer, Phys. Rev. Lett. 75, 1995, p. 97.
- [2] H.-E. Schaefer, K. Frenner and R. Würschum, Phys. Rev. Lett. 82, 1999, p. 948.
- [3] H.-E. Schaefer, K. Frenner and R. Würschum, Intermetallics 7, 1999, p. 277.

### 11:00 AM K6.2

VACANCIES IN AlPdMn: AN APPROACH BY POSITRON ANNIHILATION SPECTROSCOPY. F. Baier, M.A. Müller, A.A. Rempel, W. Sprengel, H.-E. Schaefer, ITAP, Stuttgart University, Stuttgart, GERMANY; B. Grushko, IFF, Forschungszentrum, Jülich, GERMANY.

Processes as diffusion, plastic deformation, and creep in quasicrystals are expected to be mediated by lattice defects as vacancies and phasons. The aim of the present study is to investigate to which extent techniques as positron annihilation spectroscopy [1,2] can be utilized to detect and analyse the formation of thermal vacancies at high temperatures. Investigations of other systems like intermetallic compounds (FeAl, NiAl, TiAl) showed that positron lifetime spectroscopy is a good tool for gaining information on the migration and the formation of thermal defects [3,4].

The research work presented here will focus on the investigation of icosahedral quasicrystals of the AlPdMn system. One part of the

study are the first in-situ measurements of the positron lifetime in the temperature range from room temperature up to the melting temperature  $T_M$  of the icosahedral Al<sub>70.2</sub>Pd<sub>21.3</sub>Mn<sub>8.5</sub> quasicrystal. In contrast to earlier studies[5] a reversible non-linear increase of the mean positron lifetime  $\tau_m$  from room temperature to high temperatures can be observed and is ascribed to the formation of thermal equilibrium vacancies. These vacancies can be quenched-in and subsequently annealed out.

With the assumption of a three-state trapping model we discuss the formation and migration enthalpy of this kind of thermal defect icosahedral Al<sub>70.2</sub>Pd<sub>21.3</sub>Mn<sub>8.5</sub>.

We additionally report on studies yielding information on the chemical environment of vacancies.

- [1] R. Würschum, B. Grushko, K. Urban and H.-E. Schaefer, Phil. Mag. B 70, 1994, p. 913.
- [2] H.-E. Schaefer, Phys. stat. Sol. (a) 102, 1987, p. 47.
- [3] R. Würschum, K. Badura-Gergen, E.A. Kümmerle, C. Crupp and H.-E. Schaefer, Phys. Rev. B 54 (1008) 849.
- [4] R. Würschum, E.A. Kümmerle, K. Badura-Gergen, A. Seogor, Ch. Herzig and H.-E. Schaefer, J. Appl. Phys. 80 (1996)724.
- [5] I. Kanazawa, E. Hamada, T. Saeki, K. Sato, M. Nakata, S. Takeuchi and M. Wollgarten, Phys. Rev. Lett. 79, 1997, p. 2269.

### 11:15 AM K6.3

THE EFFECT OF ELECTRONIC EXCITATIONS ON QUASICRYSTALS. Ratnamala Chatterjee, Alope Kanjilal, Physics Department, Indian Institute of Technology, Hauz Khas, New Delhi, INDIA; Annie Dunlop, Laboratoire des Solides Irradiés, CEA/Ecole Polytechnique, Palaiseau, FRANCE; O.N. Srivastava, Banaras Hindu University, Varanasi, INDIA.

Quasicrystals are metallic compositions that have no periodicity but have long range order. Electronic structure of quasicrystals is still not very well understood. Various models exist in literature, which attempt to give possible description of electrons in quasicrystals. Swift Heavy Ions (SHI) passing through materials lose energy mainly via inelastic collisions of ions with the electrons of materials.

Electronic stopping power (electronic excitations in the target material) corresponding to this inelastic collision is the dominant mechanism by which SHI lose their energy. For this very reason, SHI irradiation seems to be an attractive tool to excite the electronic structure of quasicrystals and investigate the corresponding effects on them. Preliminary work[1] on Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> stable (thermodynamically, up to ~1200K) quasicrystal done here at Nuclear Science Centre (NSC), Delhi, shows encouraging results. The beam and the energy ranges are chosen using the simulation codes SRIM-98. We have performed the experiments in the pure electronic excitation regime. In this regime, we systematically deposit various ranges of energy into the system, causing electronic excitations in them. The effect of these electronic excitations on the electronic structure of the quasicrystals are analysed by doing in-situ resistivity Vs fluence and resistivity Vs temperature measurements. Transmission Electron Microscopy and X-ray diffraction experiments are done on these irradiated samples ex-situ, to assess the structural changes, if any! For the present work we have chosen to discuss the results of the experiments done with the highly energetic 900MeV Pb beam and ~1GeV Kr beam with the electronic energy loss rate of ~3.5 to 4keV/A<sup>0</sup>. The samples (in the form of melt quenched ribbons) are irradiated at fluences of a few 10<sup>12</sup> ions/cm<sup>2</sup> in order to ensure a homogeneous irradiation. The projected range of electronic excitations were ~40 - 60 μm. The target ribbons are 25μm thick and thus the Pb and Kr beam is expected to create electronic excitation along its passage and then just pass through it. The results of the in-situ resistivity measurements and ex-situ XRD and TEM (before and after irradiation) measurements will be discussed. [1] Ratnamala Chatterjee, R.A. Dunlap and D. Kanjilal, NIM B156, 201 (1999).

### 11:30 AM K6.4

DISLOCATION AND GLIDE RESISTANCE IN MODEL QUASICRYSTALLINE LATTICE. Ryuji Tamura, Shin Takeuchi, Science University of Tokyo, Department of Materials Science and Technology, Noda, Chiba, JAPAN; Keiichi Edagawa, The University of Tokyo, Institute of Industrial Science, Komaba, Tokyo, JAPAN.

The stress necessary for dislocation glide in quasicrystals consists of two components: the phason defect production stress and the Peierls stress. We have shown by using a simple one-dimensional quasi-periodic lattice that the former stress component can be reduced to a negligible level by glide of a group of dislocations associated one another by phason faults. In the present paper, the model is extended to a more realistic, two-dimensionally quasiperiodic lattice to simulate dislocations and their glide resistance in quasicrystal. Self-energy variation of a dislocation is calculated along the dislocation line as well as along the direction of its motion. The calculated results are discussed in relation to experimental results on the plasticity of quasicrystals.

**11:45 AM K6.5**

DISLOCATION DYNAMICS IN ICOSAHEDRAL Al-Pd-Mn SINGLE QUASICRYSTALS. Ulrich Messerschmidt, Martin Bartsch, Bert Geyer, Lars Ledig, Max Planck Inst. of Microstructure Phys., Halle(Saale), GERMANY; Michael Feuerbacher, Knut Urban, Inst. Solid State Res., Res. Centre Jülich, Jülich, GERMANY.

In situ straining experiments, which directly show the dislocation motion, have been performed on Al-Pd-Mn single quasicrystals in a high-voltage electron microscope between 675°C and 765°C. Mostly, short dislocations extending from one specimen surface to the other glide on well defined planes with their line directions oriented along quasicrystallographic directions. In contrast to that, dislocations form a network in bulk specimens deformed in the same temperature range, pointing at the importance of recovery. These differences may result from the limited specimen thickness of about 0.5  $\mu\text{m}$  in the in situ experiments. The mode of dislocation motion is the same within the whole temperature range of the experiments. Dislocations moving viscously on parallel slip trails move at equal velocities. No difference can be observed between the velocity of a dislocation generating a new trace and such moving on traces formed by previous dislocations. In some cases, however, dislocations moving on traces of equal orientation and width move at velocities distinctly different by factors of more than two. A first attempt has been undertaken to determine the stress exponent of the motion of an individual dislocation by measuring its velocity under decreasing load. The data are consistent with a stress exponent of 6, which is equal to the macroscopic stress exponent of the strain rate. As a complex microstructure is not formed in the thin foils of in situ experiments, these experiments present the dynamic properties of dislocations in a temperature range where the macroscopic deformation data are controlled by recovery. The dislocation dynamics can be interpreted by models formulated on the scale of the clusters forming the quasicrystal structure. This can be either a cluster friction model in which the clusters are regarded as extended obstacles analogous to the theory of solution hardening or a Peierls model on the cluster scale.

**SESSION K7: MECHANICAL PROPERTIES**

Chair: Uwe Koester

Tuesday Afternoon, November 28, 2000

Room 203 (Hynes)

**1:30 PM K7.1**

TEMPERATURE DEPENDENCE OF DISLOCATION MOTION IN A TWO DIMENSIONAL BINARY MODEL QUASICRYSTAL: A MOLECULAR DYNAMICS STUDY. Galib Krdzalic, Hans-Rainer Trebin, Inst for Theoretical and Applied Physics, Stuttgart Univ, Stuttgart, GERMANY.

A twodimensional binary model quasicrystal (Roth-Mikulla tiling) was subjected to shear of constant rate (Lees-Edwards boundary conditions). Lennard-Jones forces were applied between the atoms and the evolution of the system was followed by isothermal molecular dynamics simulations. Temperature was controlled by a Nosé-Hoover thermostat. Dislocation dipoles were created followed by phason walls, which broadened with increasing shear. Widening happens by transversal shear induced diffusion. It starts with the onset of failure and is saturating after reaching two planes of high interface energy parallel to the glide plane. Thus a structurally damaged layer arises along which viscous glide is developing. The transverse diffusion constant follows an Arrhenius law at low temperature. With increasing temperature it is bending to a flatter slope similar as in the model of phason induced diffusion by Katz and Kalugin<sup>1</sup>. I. P.A. Kalugin and A. Katz, Europhys. Lett. 21, 921 (1993)

**1:45 PM K7.2**

MODELLING QUASICRYSTAL PLASTIC DEFORMATION BY MEANS OF CONSTITUTIVE EQUATIONS. M. Feuerbacher, P. Schall, K. Urban, IFF, Forschungszentrum Jülich GmbH, Jülich, GERMANY; Y. Estrin, IWW, TU Clausthal, Clausthal-Zellerfeld, GERMANY; Y. Breché, LTPCM, St. Martin d' Heres, FRANCE.

The interpretation of plastic deformation experiments on quasicrystals is a challenging task due to the occurrence of changes of the structure during deformation. Firstly, recovery effects influence the deformation behavior, since experiments have to be carried out at high temperatures due to the high brittle-to-ductile transition temperature of quasicrystals, and secondly, the structure of the material necessarily changes upon dislocation motion due to the lack of translational symmetry of these materials. In this paper, we present a quantitative model for quasicrystal plasticity on the basis of a constitutive-equations Ansatz, which takes these effects into account. A single-parameter equation, as commonly used for the description of crystal plasticity, is used for the description of the dislocation density. Additionally, we introduce a structural parameter, describing the

evolution of order in the course of plastic deformation. The numerical solution of the differential equation system yields the flow stress and the dislocation density as a function of strain, which can be directly compared to corresponding experimental curves obtained on icosahedral Al-Pd-Mn. Using our model, we find an excellent agreement between experimental and simulated curves. Furthermore, by solving the equation system under suitable boundary conditions, stress-relaxation experiments, strain-rate changes and creep experiments can be modeled.

**2:00 PM K7.3**

HIGH TEMPERATURE PLASTIC BEHAVIOUR OF ICOSAHEDRAL Al-Cu-Fe QUASICRYSTALS. Jan Fikar, Swiss Federal Institute of Technologie, IGA, DP, Lausanne, SWITZERLAND; Nadine Baluc, Fusion Technology Materials Division, Villigen-PSI, SWITZERLAND; Joel Bonneville, Université de Poitiers, Facultes des Sciences, Futuroscope Cedex, FRANCE; Pierre Guyot, Institut National Polytechnique de Grenoble, Domaine Universitaire, LTPCM, St Martin d'Herès, FRANCE.

Poly-quasicrystalline specimens of the icosahedral Al-Cu-Fe system have been deformed in compression at constant strain-rate in the temperature range 300-1020K. At low and intermediate temperatures, the samples are brittle and plastic deformation only takes place at temperatures above 0.7 Tm. In general the stress-strain curves exhibit after the elastic stage a marked yield drop followed by a stage of strain softening. Creep experiments were performed for various durations after interrupting the constant strain-rate deformation tests at different given stress or strain levels. After creep deformation the plastic flow was again investigated at constant strain-rate. These results can be explained in the framework of a dislocation model. Two effects are considered to oppose the dislocation motion: the usual elastic dislocation interaction, yielding a work-hardening contribution, and a friction stress specific to the quasiperiodic lattice. This friction stress is assumed to decrease with increasing strain, leading to a strain-softening effect. Integrating these two ingredients in a Kocks type viscoplastic constitutive law allows us to reproduce the stress-strain curves at constant strain-rate and the creep curves. It allows as well to understand the transition regimes observed in the interrupted composite tests. The values of the physical parameters involved in the model, deduced from the comparison with the experimental data, are finally discussed.

**2:15 PM K7.4**

LOW TEMPERATURE PLASTIC BEHAVIOR OF ICOSAHEDRAL Al-Cu-Fe QUASICRYSTALS. Nadine Baluc, Fusion Technology Materials Division, PSI, Villigen, SWITZERLAND; Joel Bonneville, Jacques Rabier, Université de Poitiers, Faculté des Sciences, Futuroscope Cedex, FRANCE.

Poly-quasicrystalline specimens of the icosahedral Al-Cu-Fe are brittle at low and intermediate temperatures: plastic deformation only takes place at temperatures above 0.7 Tm. In order to check whether pure dislocation glide can occur in quasicrystalline materials, it is of prime interest to reach plastic regimes at lower temperatures and higher stresses. Such low temperature deformation regimes can be achieved by using two techniques, which superimpose to a shear stress an hydrostatic component. These techniques, which enable to shift the brittle-to-ductile transition down to lower temperatures, are: micro indentation and deformation under confining pressure. The former technique is very easy to handle, but suffers from two main drawbacks: the stress tensor is not known and the plastified region interests a very small part of the specimen, which makes difficult the TEM observations of the deformation substructure. The latter one enables to control both deviatoric and hydrostatic stresses and allows for the measurement of the yield stress as well as the observation of the deformation microstructures in the whole sample. Such a technique has been applied to Al-Cu-Fe materials down to room temperature using gas and solid confining media. Mechanical data as well as microstructural observations obtained in this range of temperature will be discussed.

**2:30 PM \*K7.5**

FRICITION, WEAR, AND RELATED PHASE TRANSITIONS IN QUASICRYSTALS. Chuang Dong<sup>1</sup>, Jinsong Wu<sup>1</sup>, Jean-Marie Dubois<sup>1</sup>, Pierre Brunet<sup>2</sup>, Liming Zhang<sup>1</sup>, Qinggang Zhou<sup>1</sup>, Dehe Wang<sup>1</sup>, Huichen Zhang<sup>3</sup>; <sup>1</sup>State Key Laboratory for Materials Modification by Laser, Ion and Electron Beams, Department of Materials Engineering, Dalian University of Technology, Dalian, CHINA; <sup>2</sup>LSG2M, Ecole des Mines, Parc de Saurupt, Nancy, FRANCE; <sup>3</sup>Materials Research Institute, Dalian Maritime University, Dalian, CHINA.

Quasicrystalline materials find their applications mainly in surface-related fields. The most famous example is the non-stick quasicrystalline coating on cookwares which utilizes the low surface energy, high hardness, high wear and corrosion resistance, and low

friction coefficient properties. It has been noted in particular that phase transitions may occur during wear process. Therefore, phase transitions in quasicrystals are not only important to the synthesis of desired microstructures but also influences the service behavior of these materials. The present talk will cover quasicrystal-related phase transitions with emphasis on friction-related processes. We will focus on the following topics:

- (1) Phase transitions in quasicrystalline materials: Quasicrystals are formed only in certain special alloy systems via route of peritectic phase transitions. We will discuss the particularities of these transformations within the framework of phase diagram and Hume-Rothery rule.
- (2) Phase transitions in relation with friction measurement: Quasicrystals are brittle materials. However they manifest certain ductility during scratch tests. After a careful TEM examination, a scratch-induced phase transition has been observed where the quasicrystal is transformed into a bcc phase.
- (3) Relationship between quasicrystals and B2-based approximants: Some B2-based structures constitute an important group of approximants according to the  $e/a$ -constant definition of approximants. They participate phase transitions involving quasicrystals and their properties are similar to those of quasicrystals. Their structures contain also information on the local structure of quasicrystals.

#### SESSION K8: MECHANICAL PROPERTIES AND STRUCTURES - THIN FILMS

Chair: Ronan McGrath

Tuesday Afternoon, November 28, 2000  
Room 203 (Hynes)

##### 3:15 PM **K8.1**

##### THE INFLUENCE OF GRAIN ORIENTATION ON FRICTION AND WEAR BEHAVIOR IN QUASICRYSTALLINE ALLOYS.

Alan Duckham, MSEL, National Institute of Standards and Technology, Gaithersburg, MD; Dan Shechtman, Department of Materials Engineering, Technion, Haifa, ISRAEL.

The influence of grain orientation on the friction and wear behavior of single phase quasicrystalline alloys is investigated. Pin-on-disc wear tests have been performed on bulk samples of icosahedral phase AlPdMn and decagonal phase AlNiCo alloys. Friction data has been recorded during the pin-on-disc tests, while wear behavior is evaluated by optical and SEM microscopy, and EBSD analysis. Coefficient of friction values of the decagonal AlNiCo alloy are found to be widely scattered (between 0.035 and 0.55) compared to the far more consistent values of the icosahedral alloys. This is explained by considering the significant variation in wear behavior that is observed between different - sometimes adjacent - oriented grains in the decagonal specimens.

##### 3:30 PM \***K8.2**

OXIDATION AND FRICTION STUDIES OF AlPdMn QUASICRYSTALS AND ITS APPROXIMANT Al<sub>48</sub>Pd<sub>42</sub>Mn<sub>10</sub>. Andrew Gellman, Chris Mancinelli, Jeff Ko, Dept of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA.

Fundamental studies in an ultra-high vacuum environment have been conducted to probe the dependence of surface structure on the oxidation and friction of quasicrystal materials and their approximants. Quasicrystals are materials that have very complex, aperiodic structures with five-fold rotational symmetry, and they have been found to exhibit low friction and adhesion as well as high wear resistance. Our experiment allows us to make friction measurements between pairs of well-prepared and highly characterized surfaces that are brought into contact under an applied load and then sheared relative to each other at a constant velocity. Oxidation kinetics studies performed on a pair of Al<sub>70</sub>Pd<sub>21</sub>Mn<sub>9</sub> quasicrystals and one of its approximants, Al<sub>48</sub>Pd<sub>42</sub>Mn<sub>10</sub>, have revealed a difference in oxygen uptake kinetics between the two alloys. The approximant appears to oxidize at a much faster rate compared to the quasicrystal. The frictional properties of the quasicrystal approximant, Al<sub>48</sub>Pd<sub>42</sub>Mn<sub>10</sub>, which has a CsCl-type structure, have been compared to those of its quasicrystalline counterpart, icosahedral Al<sub>70</sub>Pd<sub>21</sub>Mn<sub>9</sub>. In friction experiments between two quasicrystalline samples, a decrease in friction with increasing oxidation of the samples was observed. The effect of quasicrystal composition on its low friction behavior is important to formulation of effective non-stick, wear-resistant coatings and other such applications.

##### 4:00 PM \***K8.3**

QUASICRYSTALLINE FILMS. R. Haberkern, J. Barzola-Quiquia, C. Madel, K. Khedhri, M. Lang, P. Häussler, Institut für Physik, TU Chemnitz, Chemnitz, GERMANY.

We report about the preparation of quasicrystalline films via the route of the amorphous state. Hereby, homogeneous amorphous films are deposited at room temperature or at  $T=4$  K by the technique of sequential-flash evaporation in the case of Al-Cu-Fe and Al-Pd-Mn and by sputtering in the case of Al-Pd-Re. All systems mentioned can be transformed into the quasicrystalline state by a heat treatment at comparably low temperatures and short times (e.g.  $\sim 10$  minutes at 430°C for Al-Cu-Fe). In situ measurements of electronic transport properties (electrical conductivity, thermopower) were used to optimize the annealing procedures and to investigate the occurrence of crystalline intermediate phases as a function of composition. The resulting icosahedral films are characterized by TEM and electronic transport properties (thermopower, Hall-effect, conductivity) in the temperature range from 1.3 to 1000 K. From the composition- and temperature dependence of the transport properties the spectral conductivity  $\sigma(E)$  can be modeled which relates all transport properties to each other. This is helpful to design icosahedral films for technical applications as for example as thermoelectric materials.

##### 4:30 PM **K8.4**

AN INVESTIGATION OF SPUTTERED Al-Cu-Fe-Cr QUASICRYSTALLINE FILMS VIA SYNCHROTRON DIFFRACTION. M.J. Daniels, S.M. Yalisove, J.C. Bilello, Center for Nanomaterials Science, Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI; J. Maciejewski, Technology Assessment and Transfer, Annapolis, MD; J.S. Zabinski, Air Force Research Lab, Wright-Patterson Air Force Base, OH; Z.U. Rek, Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, CA.

The phase structure of Al-Cu-Fe-Cr sputtered films, before and after various annealing treatments, was carried out via grazing incidence x-ray scattering (GIXS) at SSRL on beamline 7-2. The as-deposited films were primarily amorphous in character and the annealing treatments converted them, in varying degrees, to quasicrystalline microstructures. GIXS studies, in the symmetric and asymmetric modes, revealed that the decagonal QC phase (primarily) plus other quasicrystalline phase resulted from these post-deposition heat treatments. These nominally 10 micron thick films were created by sputter deposition with an RF magnetron source using Al-Cu-Fe-Cr powder pressed targets designed to produce a nominal coating composition 71.7%Al-5%Cu-11.3%Fe-12%Cr. Two annealing treatments were performed in argon atmosphere. The GIXS studies reveal that anneals of the precursor amorphous films at 500°C for 4 hours produced approximately 0.60 volume fraction decagonal QC phase. Annealing at 400°C for 2 hours followed by an additional 2 hours at 550°C produced a lower fraction of decagonal QC phase. Two additional phases are also present and correspond to another QC phase plus a crystalline phase and the quantitative aspects of these are currently under investigation. The results show that relatively stable quasicrystalline coatings can potentially be prepared via sputter deposition methods.

Acknowledgments: Work performed, in part, under U.S. DoD - Dept. of Air Force contract number F0011539 and thanks also to U.S. DoE for support of research done at SSRL under proposal no. 2592

##### 4:45 PM **K8.5**

MORPHOLOGY OF SPUTTERED Al-Cu-Fe-Cr QUASICRYSTALLINE COATINGS. M.J. Daniels, S.M. Yalisove, J.C. Bilello, Center for Nanomaterials Science, Department of Materials Science and Engineering, University of Michigan, Ann Arbor MI; J. Maciejewski, Technology Assessment and Transfer, Annapolis MD; J.S. Zabinski, Air Force Research Lab, Wright Patterson Air Force Base OH; Z.U. Rek, Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford CA.

The morphology of Al-Cu-Fe-Cr sputtered films, before and after various annealing treatments, was studied by SEM, AFM, and plan-view TEM. Two types of substrates were used in the present work, Si(100) wafers and alumina polycrystalline blanks. These films were nominally 10 microns thick. Annealing treatments produced films that were primarily decagonal phase with a variety of resultant morphologies. A striking difference in the final state was observed in comparing the Si with alumina substrates. In the latter case, crack nucleation initiated at voided regions, which had geometry that displayed sharp features. The crack growth followed transgranular paths in the films coated on alumina. Results will be presented which will correlate the residual stresses (determined from x-ray methods), phase, composition, and morphology of these films. Acknowledgments: Work performed, in part, under U.S. DoD - Dept. of Air Force contract number F0011539 and thanks also to U.S. DoE for support of research done at SSRL under proposal no. 2592.



#### **K9.1**

**CORROSION RESISTANCE IN CITRIC ACID OF Al-BASED QUASICRYSTALS AND RELATED CRYSTALS.** Lionel Aranda, Christophe Rapin, Pierre Steinmetz, Université Henri Poincaré, Nancy, FRANCE; Marie-Cecile de Weerd, Pierre Brunet, Jean-Marie Dubois, Ecole des Mines, Nancy, FRANCE; Daniel J. Sordelet, Ames Laboratory and Iowa State University, Ames, IA.

A major concern in view of the application of quasicrystalline materials to coating cooking utensils is their resistance to corrosion. We present here new results about the corrosion resistance of a number of quasicrystals and approximant materials in electrolytes frequently encountered in the environment of a kitchen, namely water from the tap and citric acid (contained for instance in tomatoes). The influence of Cl ions from NaCl is also studied. The results are put in the perspective of a comparison to austenitic stainless steel. It turns out that the addition of Cr to the Al-Cu-Fe base quasicrystal improves significantly the corrosion resistance of the materials, although pitting is not entirely suppressed in the presence of NaCl. Ways to improve further the corrosion resistance of the quasicrystalline materials are addressed.

#### **K9.2**

**TRANSFORMATIONS OF Al-Cu-Fe ATOMIZED POWDERS UPON ANNEALING AT 500°C.** Patrick Weisbecker, Li-Ming Zhang, Aurelie Call, Galtan Bonhomme, Jean-Marie Dubois, Laboratoire de Science et Genie des Matériaux Metalliques (UMR 7584 CNRS-INPL), Ecole des Mines, Nancy, FRANCE.

The industrial route towards the production of thick coatings of quasicrystalline materials supposes the preparation in a first step of spherical atomized powders. Such powders experience upon solidification drastic cooling rates and therefore are quenched-in at room temperature in a metastable state. They form spherical particles, broadly distributed in size, with diameters ranging from a few nm to about 200 nm. Particles useful for plasma spray are selected in a much narrower range, typically (-45, 65 nm). They usually comprise at least three phases, namely the icosahedral compound, the b-cubic iron-rich Al-Cu-Fe phase trapped from the high temperature region and another B2-type t-cubic phase which forms later upon cooling and contains essentially little Fe. After others (1), we have studied the transformation path from metastable atomized powder towards the equilibrium state during annealings at 500°C either under vacuum or in dry air. Based on the preparation of well defined b-cubic samples of known stoichiometry and the evolution of their lattice parameter with composition, we trace for the first time the variation of the constituent concentrations with duration of anneal. An Avrami analysis of Bragg peak intensities yields informations about the mechanism of the transformation. Finally, we show evidence that oxygen not only contributes to the formation of an oxide surface layer but also penetrates into the icosahedral lattice. 1-D.J. Sordelet et al., in *New Horizons in Quasicrystals*, eds. A.I. Goldman et al. (World Scientific, Singapore, 1997), p. 296; S.M. Lee et al., preprint (2000), submitted to JMR.

#### **K9.3**

**FORMATION OF Mg-Al-TM (TRANSITION METAL) QUASICRYSTALS.** Naokiyo Koshikawa, Shinichi Yoda, National Space Development Agency of Japan, Ibaraki, JAPAN; Tokyo Institute of Technology, Dept of Innovate and Engineered Materials, Kanagawa, JAPAN; Keiichi Edagawa, Univ of Tokyo, Institute of Industrial Science, Tokyo, JAPAN; Shin Takeuchi, Science Univ of Tokyo, Chiba, JAPAN.

After discovery of stable FK-type and metastable MI-type quasicrystals in the Mg-Al-Pd system, some new quasicrystals in Mg-Al-TM (Transition Metals) were found. In this report, the results of Pd substitution in Mg-Al-Pd system by other transition metal elements are shown. Our previous experiments showed, for instance, the formation of MI-type Mg-Al-Rh quasicrystal. In this presentation, emphasis is focused on evaluating the relationship among the atomic radius, the valence electron concentration per atom ( $e/a$ ), and the phase formation. Mg-Al-TM samples were prepared by using an arc melting furnace. The quenched samples were obtained by a melt spinning method. Afterwards, the samples are examined by X-ray powder diffraction.

#### **K9.4**

**THE THERMAL STABILITY OF A SINGLE-GRAIN Mg-Zn-Y ICOSAHEDRAL QUASICRYSTAL.** Z.P. Luo, Y.L. Tang, D.J. Miller, Argonne National Laboratory, Materials Science Division, Argonne,

IL; M.J. Kramer, I.R. Fisher, Ames Laboratory, Iowa State University, Ames, IA.

It is currently believed that the Mg-Zn-RE (RE: rare earth) quasicrystals are thermodynamically stable, since they are formed from the melt directly upon slow solidification. However, their thermal stability has not yet been well studied due to the presence of secondary crystalline phases in polycrystalline materials. In this work, the stability of Mg-Zn-Y icosahedral quasicrystal (IQC) was studied using a single large grain. This single grain was crushed to yield small fragments which were then sealed individually into quartz tubes for annealing studies to evaluate the stability of the IQC. At 773 K for an annealing time of 1500 h, the IQC is still the predominant phase, while the quasilattice parameter is contracted from 0.5200 nm to 0.5183 nm. However, it was found that the IQC is not stable during extended annealing at high temperatures. At 823 K for 720 h or 873 K for 300 h, the IQC is completely decomposed to various crystalline phases. A new cubic Mg-Zn-Y approximant has been found in the annealed samples. It is a face-centered cubic (fcc) structure with lattice parameter of  $a = 1.276$  nm, which is about  $(1/\tau)$  times smaller than that of the fcc  $W'$  with  $a = 2.05$  nm reported previously, where  $\tau$  is the golden ratio (1.618...). The detailed decomposition kinetics and related crystalline structures will be presented.

#### **K9.5**

**FORMATION OF THE GAMMA-BRASS STRUCTURE IN A SIMPLE MONATOMIC LIQUID.** F. Zetterling and M. Dzugutov, Dept of Numerical Analysis and Computer Science, Royal Institute of Technology, Stockholm, SWEDEN; S. Lidin, Dept of Inorganic Chemistry, Stockholm University, Stockholm, SWEDEN.

Phase transformations in simple systems with the topological local order involving icosahedral coordination of the first shell of neighbours attract much research activity. Because of the frustration inherent to the icosahedra packing in the flat 3D space the unit cells of the periodic structures involving icosahedral structural units must also include non-icosahedral defects. This leads to a huge variety of phases with very complicated geometry. In the real world, these phases are typically formed by multicomponent intermetallic systems, but there are examples of icosahedral elemental structure induced by strong bonding (B, Mn). It is important to discriminate the role of the topological ordering in formation of these phases from that of the chemical ordering which inevitably arises in multicomponent systems. Therefore, the question of whether the formation of a periodic phase with icosahedral local order can be induced by a spherically symmetric pair potential in a system composed of one sort of atoms is of profound conceptual interest. In this report, we present a molecular dynamics simulation where a simple monatomic liquid with the icosahedral short-range order induced by the design of the pair potential forms under cooling the gamma-brass structure, a periodic phase observed for example in CuZn alloy which confines 8 icosahedra in its 52-atom unit cell.

#### **K9.6**

**CLUSTER STRUCTURES AS MODELS FOR THE STRUCTURE OF QUASICRYSTALS AND APPROXIMANTS.** Hartwig Schlueter, Schlueter Consult, Kaufungen/Hess., GERMANY.

Mackay-type and Bergman-type clusters are used for modelling structures of quasicrystals and approximants. As a characteristic feature of these structures, nearest neighbour clusters have coincidence sites and a common 2-, 3- or 5-fold symmetry axis. The coincidence sites lead to a directional bonding of nearest neighbour clusters. For the cubic and rhombohedral approximant models, the models for icosahedral quasicrystals and one special decagonal quasicrystal and its related monoclinic approximant, the symmetry axes of the clusters have the same orientation. In the models for all the other decagonal quasicrystals and their related monoclinic approximants, there are two distinct orientations of the clusters. Similarities between the cluster structures of decagonal and icosahedral quasicrystals will be shown and the plausibility of the cluster models is checked by comparison of x-ray diagrams and HRTEM-images with simulated ones. During their growth, approximants and quasicrystals are seen mainly as structures, where clusters organize themselves according to certain rules rather than being self-organized atomic structures. Via coincidence sites, the existing clusters define how to match the emerging clusters to the structure at the time of formation. Furthermore, possible cluster structures in amorphous alloys will be discussed in relation to the cluster structures of quasicrystals. Results from transport measurement in thin amorphous and quasicrystalline layers give evidence for such a relation.

#### **K9.7**

**THE MODEL FOR ICOSAHEDRAL Al-Pd-Mn BASED ON THE CANONICAL, FROM D6 PROJECTED TILING.** Gerald Kasner, Zorka Papadopolos, Otto-von-Guericke Universität, Institut für Theoretische Physik, Magdeburg, GERMANY.

The icosahedral canonical tiling composed of 6 golden tetrahedra of the 3-dimensional space is decorated for physical applications using the alternating Bergman and Mackay polytopes [1,2]. In our model [2], not only the Fibonacci like sequences are possible. The inclusion of the shortest distance of 2.52 Å breaks the Fibonacci-sequence of terrace like surfaces. These three distances among the terraces (mutually scaled by a factor  $\tau$ ) have been recently observed by the Iowa Group [3]. We predict the frequencies of the appearance of the terraces in the model. According to the "spherical" model of de Boissieu et al, we decorate the atomic positions by Al, Pd and Mn. We give images of the predicted terrace-like surfaces on 3 possible distances decorated by the atomic species. [1] V. Elser, *Philos. Mag.* B 73, 641 (1996) [2] G. Kasner, Z. Papadopolos, P. Kramer and D. Bürgler, *Phys. Rev. B* 60, 3899 (1999) [3] Z. Shen, C.R. Stoldt, C.J. Jenks, T.A. Lograsso, and P.A. Thiel, *Phys. Rev. B* 60, 14688 (1999)

**K9.8**  
LOCAL SYMMETRY OF DECAGONAL QUASICRYSTALS STUDIED BY ELECTRON MICROSCOPY. Eiji Abe and An Pang Tsai; National Research Institute for Metals, Tsukuba, JAPAN.

Alternative to previous symmetric cluster description of quasicrystals, the structure has been shown to be a result of simple decoration of Penrose tiling; the quasicrystal symmetry is that of the Penrose tiling. Now the focusing issue is a local symmetry of the decagonal quasicrystals, namely, the true symmetry of the symmetric-cluster-like region observed so far in the high-resolution transmission electron microscopy (HRTEM) images. To clarify this, we successfully employ the through-focus HRTEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). Chemical ordering of the structure is derived from HAADF-STEM with Z-contrast (Z: atomic number) highlighting the heavy atom position. Details on a total atomic arrangement including relatively light constituent elements and its local symmetry are investigated by through-focus HRTEM with phase contrast. On the basis of these observations, the symmetry-breaking of the 2nm-cluster is due to arrangement of both Al and transition-metal atoms for the Al-Ni-Co, while that is due to only Al displacements from 10-fold symmetric positions for the Al-Mn-Pd. A possible local chemical ordering, Ni/X, is discussed by a successful substitution for the Co site by a heavier X element that would lead to a highly perfect Al-Ni-X decagonal phase. The present results demonstrate that a combination of HRTEM and HAADF-STEM is quite powerful for complicated intermetallic structures, convincing a reliable structural analysis based on electron microscopy.

**K9.9**  
REFINEMENT OF d-Al-Ni-Co QUASICRYSTAL STRUCTURES. Hiroyuki Takakura<sup>1,2</sup>, Akiy Yamamoto<sup>3</sup>, An Pang Tsai<sup>1</sup>; <sup>1</sup>National Research Institute for Metals, Tsukuba, JAPAN; <sup>2</sup>CREST, Japan Science and Technology Corp., Kawaguchi, Saitama, JAPAN; <sup>3</sup>National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

A decagonal Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub> (d-Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub>) has a 0.4nm period along the 10-fold axis. It shows no satellite reflections in contrast to Co rich d-Al-Ni-Co quasicrystals and has no diffuse layer indicating some disorder related with a 0.8nm period, which is usually observed in this quasicrystals. Therefore this is considered to be a basic structures for understanding a series of Al-Ni-Co quasicrystal structures. Since d-Al<sub>72</sub>Ni<sub>20</sub>Co<sub>8</sub> is stable, sub-millimeter-sized single crystals are available. Single-crystal x-ray diffraction measurements were carried out on four-circle diffractometer equipped with Mo-K $\alpha$  radiation. The sample was polished into an ellipsoid with about 0.22 mm in diameter. The reflections within 3/40 region in the reciprocal space were measured and 451 independent reflection intensities ( $\geq 3\sigma$ ) were obtained after the absorption correction. The structure refinements were carried out on the basis of two cluster models with the space group  $P10_5/mmc$ , which are modifications of models proposed by one of the author (A.Y.) and Saitoh *et al.*<sup>1,2</sup> The two earlier models proposed by Burkov and Yamamoto are also tested to compare the results.<sup>3,4</sup>

<sup>1</sup>A. Yamamoto, K. Kato, T. Shibuya, and S. Takeuchi, *Phys. Rev. Lett.*, **65**, 1603 (1990).  
<sup>2</sup>K. Saitoh, K. Tsuda, M. Tanaka, K. Kaneko, and A.P. Tsai, *Jpn. J. Appl. Phys.*, **36**, L1400 (1997).  
<sup>3</sup>S.E. Burkov, *Phys. Rev. Lett.*, **67**, 614 (1991).  
<sup>4</sup>A. Yamamoto, *Sci. Rep. RITU*, **A42**, 207 (1996).

**K9.10**  
ALUMINUM-BASED QUASICRYSTALS STUDIED BY SLOW POSITRON BEAM TECHNIQUE. K. Sato, H. Uchiyama, I. Kanazawa, Department of Physics, Tokyo Gakugei University, Tokyo, JAPAN; R. Tamura, K. Kimura, Department of Materials Sciences, The University of Tokyo, Tokyo, JAPAN; F. Komori, Institute for Solid State Physics, The University of Tokyo, Tokyo, JAPAN; R. Suzuki, T. Ohdaira, Quantum Radiation Division, Electrotechnical

Laboratory, Ibaraki, JAPAN; S. Takeuchi, Department of Materials Science and Technology, Science University of Tokyo, Chiba, JAPAN.

Recently, many proposals have been reported for an atomic cluster model of Al-based icosahedral quasicrystals, e.g. i-AlCuFe, i-AlLiCu, i-AlPdMn, etc., by single-crystal X-ray diffraction analysis, single-crystal neutron diffraction analysis, and high resolution transmission electron microscopy and so on. However unified view of the structure has not yet been obtained because of the lack of quantitative experimental data. As one of the reasons for this, a quasi-periodic structure of the quasicrystals is mentioned. Positron-annihilation methods overcome this disadvantage, and carry information such as electronic state, vacancy, diffusion, and more potentially Fermi level about quasicrystals. We have already indicated by positron-annihilation method that many kinds of stable quasicrystals contain a dense distribution of structural vacancy-type sites. For instance, in i-AlLiCu, i-AlPdMn, i-AlCuFe, and i-AlCuRu, it has been clarified that most positrons are trapped at intrinsic structural vacancies. Especially, in the case of plastically deformed i-AlPdMn alloys, no additional lifetime component could be detected, because the structural vacancy density is so high that the detection of an effect of dislocations on the positron lifetime which is usually observed in crystalline metals is hindered. Now that we confirm that stable icosahedral quasicrystals contain a dense distribution of structural vacancy-type sites, the next step is to determine the structural vacancy densities in quasicrystals. In this study, Al-based quasicrystals were investigated by means of slow positron beam technique. The results indicated that every sample contains a dense distribution of structural vacancy-type sites. In addition, the structural vacancy densities in quasicrystals were successfully determined.

**K9.11**  
PROCESSING AND MECHANICAL PROPERTIES OF QUASICRYSTAL-REINFORCED Al-ALLOYS. Frank Schurack, Jürgen Eckert, Ludwig Schultz, Institut für Metallische Werkstoffe, IFW Dresden, GERMANY.

We investigated the suitability of powder metallurgy as well as injection moulding as fabrication routes for light-weight Al-based composites with quasicrystalline particles embedded in aluminium as matrix component. Powder was synthesized by milling appropriate elemental powder mixtures or arc-melted prealloys using a planetary ball mill and an attrition mill. The mixture of the quasicrystalline and the Al-matrix phase at an appropriate ratio was realized by an excess of aluminium compared to the quasicrystal composition in the initial powder or by blending of quasicrystalline powder with pure aluminium which results also in a different evolution of the microstructure of the composite. The powders were consolidated by isothermic hot pressing and extrusion. Furthermore, bulk samples were directly prepared by squeezing the melt into a copper-mould. XRD and TEM investigations revealed a homogeneous microstructure with grain sizes ranging from 10 to 50 nm for both, the quasicrystals and the aluminium phase in the powder samples milled with an initial aluminium excess but a more heterogeneous distribution of microcrystalline particles in the matrix in blended powders. The microstructure of the cast rods is characterized by globular shaped micrometer-sized grains of isolated quasicrystals in the matrix phase. CERT-compression tests revealed with yield strengths of about 400 MPa, ultimate strengths of around 600 MPa and ductilities of up to 20% fracture strain optimum mechanical properties. As a function of the volume fraction of the components and of the composite microstructure the mechanical properties can be tailored within a wide range concerning strength and strain.

**K9.12**  
INVESTIGATION OF MECHANICAL PROPERTIES AND PHASE TRANSITION OF Al-Cu-Fe QUASICRYSTAL BY MICRO- AND NANO-INDENTATION TECHNIQUE. Yuly V. Milman, Dina V. Lotsko, Anton N. Belous, Institute for Problems of Material Science, Kiev, UKRAINE; Sergey N. Dub, Institute for Superhard Materials, Kiev, UKRAINE.

In connection with high microscopic brittleness mechanical properties of quasicrystals (yield stress in particular) were studied earlier only at temperatures higher than 0.8-0.85 Tm (873K for Al63Cu25Fe12 alloy). In the presented work with using the methods of the estimation of mechanical properties by indentation developed by the authors there were studied mechanical properties of AlCuFe quasicrystal in a wide temperature interval (77-1073K), especially at room temperature. By the technique of indentation with using a set of pyramid indenters with various angles at the tip there were constructed the deformation curves in the coordinates average contact pressure (Meier hardness) - degree of plastic deformation. It is shown that at room temperature as well as at high temperatures plastic deformation of a quasicrystal leads to its intensive softening. The annealing of deformed quasicrystal leads to the increase of hardness and yield stress. In the

curve of the temperature dependence of the hardness HV in the temperature interval 77-600K there was revealed a region with a weak dependence HV(T). It was established that in this temperature region the indentation leads to the transition under the indenter of the quasicrystal into more plastic crystalline phase and its extrusion from under the indenter. While nanoindentation such extrusion occurs repeatedly that leads to a stepped character of the loading curve. The tongues swelled by the indenter were observed by SEM technique. In the region of temperatures higher than 0.8Tm the phase transition under the indenter occurs only in its central part of indentation where stress concentration is high. With the increase of temperature the relative area of the indentation in which the phase transition takes place is lowered. There is discussed the change of mechanical properties (strength and plasticity) in a wide temperature interval.

#### K9.13

STUDIES ON SYNTHESIS AND MICROHARDNESS TESTING OF NANO-QUASICRYSTALLINE ALLOY IN  $Ti_{153}Zr_{27}Ni_{20}$  SYSTEM. M.A. Shaz, Dept of Physics, N.K. Mukhopadhyay, R.K. Mandal, Dept of Metallurgical Engineering, O.N. Srivastava, Dept of Physics, Banaras Hindu University, Varanasi, INDIA.

We present here the synthesis of nano-quasicrystalline(QC) phase in the melt spun ribbons of  $Ti_{153}Zr_{27}Ni_{20}$  alloy based on results of X-ray diffraction (XRD) and transmission electron microscopy(TEM). We shall also report the studies of microhardness testing by Vickers hardness technique, in order to understand the mechanical response. Nano-icosahedral quasicrystalline(IQC) phase was formed by employing melt-spinning of alloy at a wheel speed of 40 m/s. The nano-IQC phase of 30 to 40 nm size was monitored through broadening of XRD peak and also detected through diffraction monitored by 30 nm electron probe, using TEM. Along with this IQC phase, other crystalline phases (<100nm) were also found to co-exist. These crystalline phases were found to be belonging to cubic crystal system with  $a=3.4\text{\AA}$  and other one to be a hexagonal phase with  $a=5.21\text{\AA}$  and  $c=8.53\text{\AA}$ . The percentage of nano-IQC phase was found statistically from the observation under TEM on various locations. It was estimated that more than 75% of the phase are of IQC type. The hardness of alloy was found to be  $\sim 3.6\text{GPa}$ . When comparing the hardness of QC phase in other Al based systems, it is noticed that hardness value in nearly three times less than the reported hardness ( $\sim 9\text{GPa}$ ). It is interesting to note that there are no cracks observed with indentation upto the load of 100g. At 200g load, the linear cracks are found to initiate from the corners of the indentation. Some of the corners are free from the cracks. It must be emphasised that all the QC so far reported exhibit microcracking under indentation testing. In the present case, the absence of cracks at lower load obviously indicates better toughness of nano-QC material. This can be attributed to the nano-structure formation of IQC-phase. Attempts will be made to discuss the results in the framework of nano-QC phase formation and its typical mechanical response similar to the case of nano-crystalline phases.

#### K9.14

ESTIMATION OF BACK STRESS PRODUCED BY DISLOCATION INTERACTION IN ICOSAHEDRAL Al-Pd-Mn. Hisatoshi Hirai, Akira Kitahara, Kyushu National Industrial Research Institute, Tosu, Saga, JAPAN; Fuyuki Yoshida, Hideharu Nakashima, Kyushu Univ, Graduate School of Engineering Science, Kasuga, Fukuoka, JAPAN.

High-temperature deformation of icosahedral Al-Pd-Mn is known to be brought about by viscous motion of dislocations, and the back stress ( $\sigma_i$ ) of deformation is estimated to be 20 to 30% of applied stress. In the deformed specimen, complicated dislocation microstructure and junctions supposed to be made by the attractive reaction of dislocations are observed. Recently, dislocation reactions in icosahedral Al-Pd-Mn were theoretically investigated in detail and revealed that there are many possible attractive reactions to make the junction. Some of the proposed reactions were confirmed to exist experimentally. In this paper, we try to calculate the breakaway stress ( $\sigma_b$ ) of dislocation from the attractive junction, and compare it with the observed  $\sigma_i$ . Assuming that the force  $f$  acting on the unit length of a dislocation with the Burgers vector  $\mathbf{b}$  under a shear stress  $\tau$  is  $f = \tau |\mathbf{b}_{\parallel}|$  where  $\mathbf{b}_{\parallel}$  is the phonon component of  $\mathbf{b}$ , and that elastic energy per unit length of a dislocation  $W$  is approximated by  $W = G(|\mathbf{b}_{\parallel}|^2 + c|\mathbf{b}_{\perp}|^2)$  where  $G$  is the shear modulus,  $\mathbf{b}_{\perp}$  the phason component of  $\mathbf{b}$  and  $c$  a coefficient of about  $3.1 \times 10^{-3}$ . Using the measured dislocation density of  $1.8 \times 10^{13} \text{ m}^{-2}$ ,  $G = 48.4 \text{ GPa}$  at 1070 K and the Taylor factor  $M = 3$  in conjunction with the above assumptions, we calculate  $\sigma_b$  for 21 possible dislocation reactions. Picking up the seven most realistic dislocation reactions, the  $\sigma_b$  distributes between 50 and 140 MPa, and the average of them is about 75 MPa. The order of the calculated  $\sigma_b$  coincides the measured  $\sigma_i$  well, although our calculation of  $\sigma_b$  is only preliminary. The result above strongly suggests the possibility that the  $\sigma_i$  of the high-temperature deformation of icosahedral Al-Pd-Mn is explained by the  $\sigma_b$ .

#### K9.15

MAGNETRON SPUTTERING OF Al-Cu-Fe THIN FILM COATINGS. Daniel Sordelet, Matthew Besser, Ames Laboratory, Department of MS&E, Iowa State University, Ames, IA; Frank Kustus, Engineered Coatings, Inc., Parker, CO.

A feasibility study was performed to synthesize quasicrystalline coatings via magnetron sputtering. The targets for sputtering were prepared by plasma arc spraying of gas atomized Al-Cu-Fe powders. The influence of working gas (Ar) pressure, substrate bias, substrate temperature, and substrate material on the composition and structure of the coatings was examined. Coatings deposited onto ambient temperature Ni-based alloy substrates were typically amorphous. Post deposition annealing did lead to formation of an icosahedral phase as long as the coating composition was close to the starting composition of the plasma sprayed sputtering target. The results from preliminary experiments to fabricate composite thin film coatings comprised of an Al-Cu-Fe quasicrystalline matrix containing a uniformly distributed Fe-Al phase will also be discussed.

#### K9.16

THE LOCALIZATION AND PSEUDO-GAP IN THE QUASICRYSTAL-LIKE SYSTEM. Ikuzo Kanazawa, Tokyo Gakuji Univ, Dept of Physics, Tokyo, JAPAN.

In several idealized approximants of quasicrystals, the band calculations show the presence of the pseudogap around the Fermi energy (1). These pseudogaps may be widened and deepened by aggregation of icosahedral clusters (2). It is suspected that the correlated clusters connected with the distance  $\approx 2\pi/2k_F$  play an important role in the transport property of quasicrystals. Recently the present author (3) has considered the transport property in the randomly distributed system of the correlated clusters with the distance  $\approx 2\pi/2k_F$  (the quasicrystal-like system). G. Trambly de Laissardiere et al(4) proposed the importance of the sp-d hybridisation in the clusters of the transition metals in the transport property of quasicrystals. In the present study, we shall consider the transport property in the randomly distributed system of the correlated clusters with the distance  $\approx 2\pi/2k_F$  in the Feynman graph of Langer-Neal correction(5), taking into account the sp-d hybridisation. (1) T. Fujiwara, Phys. Rev. B40 (1989) 942. (2) C. Janot, Phys. Rev. B53 (1996) 181. (3) I. Kanazawa, Physica B, in press (2000). (4) G. Trambly de Laissardiere, D. Mayou and D. Nguyen Manh, Europhys. Lett. 21 (1993) 319. (5) J.S. Langer and T. Neal, Phys. Rev. Lett. 16 (1966) 984.

#### K9.17

INFLUENCE OF CHEMICAL DISORDER, PHASON FLIPS AND MAGNETIC FIELD ON THE LOCALIZATION OF ELECTRONIC STATES IN A REGULAR ICOSAHEDRAL QUASICRYSTAL. S.F. Arslanov, E.I. Isaev, Yu. Kh. Vekilov, Moscow State Institute of Steel and Alloys, Theoretical Physics Department, Moscow, RUSSIA; Mikhail I. Mendeleev, Princeton Univ, Princeton, NJ.

In a regular perfect quasicrystal electronic states at the Fermi level are localized due to their coherent interference at the Fermi level which is caused by the specific symmetry (properties) and aperiodic long-range atomic order. Electronic spectrum contains a singular part and has a spiky character. Wave functions are "critical". Investigation of small perturbations (phasons, magnetic field, chemical disorder) shows that the electron localization in quasicrystals is not of Anderson type which is typical for the disordered systems and in contrast to Anderson localization their influence is more pronounced at the band center. Phasons smooth the electronic spectrum and produce a greater delocalization of the "critical" wave functions. A magnetic field shifts the boundaries of the spectrum, smoothes the spectrum and lifts its degeneracy. At small magnetic fields ( $\lambda_H > a_{qt}$ ,  $\lambda = \sqrt{\hbar c / eH}$ , where  $\lambda$  is magnetic length,  $a_{qt}$  - quasilattice parameter) the wave functions become more delocalized. So at fields  $H < 10 T$  and very low temperatures the magnetoresistance of pure perfect quasicrystal should be negative. The influence of chemical disorder was studied in the single - band model for the two - component random alloy. The small degree of the chemical substitutional disorder disturbs the phase coherence of the wave functions and makes them more delocalized. But further increase of disorder leads to the Anderson type of localization, and the new localized states appear.

#### K9.18

FIRST RESULTS ON THE ELECTRONIC DISTRIBUTIONS OF Mg-Zn-Y ALLOYS AS INVESTIGATED WITH SOFT X-RAY SPECTROSCOPIES. Esther Belin-Ferré, Vincent Fournée, Marie Francoise Fontaine, LCPMR, UMR 7614, Paris Cedex, FRANCE; Anne Sadoc, LPMS Université de Cergy-Pontoise, Cergy-Pontoise Cedex, FRANCE; Herbert Mueller, Institute for Experimental Physics, TU Wien, Wien, AUSTRIA; An Pang Tsai, NRIM, Tsukuba, JAPAN.

We report our preliminary results on the electronic structure of  $Mg_{35}Zn_{25}Y_{10}$  icosahedral quasicrystal as compared to crystalline alloys, namely hexagonal  $Mg_{28}Zn_{65}Y_7$  and  $MgZn_2$ . We have used Soft-X-ray Spectroscopy techniques as it is well known that they allow one to study local partial densities of states. The occupied Mg 3s,d, and Mg 3p states have been investigated using Soft X-ray Emission Spectroscopy measurements, whereas thanks to Soft X-ray Absorption experiments we have probed empty Mg p, Zn d-s and Y d-s states, respectively. The various sub-bands are adjusted in the binding energy scale in order to have a view of both occupied and unoccupied bands and also to discuss the electronic interactions in these compounds with emphasis put on the role of Y.

#### **K9.19**

**PHASE TRANSFORMATION AND ELECTRICAL RESISTIVITY OF Al-Pd-(Ru,Os) I-PHASES.** Takayuki Asao, Ryuji Tamura and Shin Takeuchi, Science Univ of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN.

We have previously reported that in the Al-Pd-Ru and Al-Pd-Os systems, well ordered I-phases can be produced by annealing melt-quenched samples at 1273K for 1 to 24 hours. These I-phases are considered to be metastable and they transform into a 1/0 cubic approximant phase for a prolonged annealing time. Since the I-phases in these systems are quite stable and well ordered, it is interesting to make a direct comparison of the electrical and thermal properties between the I-phase and the approximant phase at the same composition. The stability of the I-phases and the transformation behavior have been studied by means of DSC, X-ray diffraction and electron diffraction measurements. Results of the electrical resistivity and specific heat measurements will also be presented.

#### **K9.20**

**AC CONDUCTION IN QUASIPERIODIC LATTICES.** Chumin Wang, R. Oviedo-Roa, V. Sanchez and L.A. Pérez, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México DF, MEXICO.

The electronic transport in Fibonacci lattices at zero temperature is studied by means of the Kubo-Greenwood formula and within the tight-binding scheme. A new renormalization method capable to address the electrical conductivity in macroscopic quasiperiodic systems is developed. The effects of the boundary conditions on the ac conductivity are analyzed for a wide range of the system sizes. The results show a rapid decay of the conductivity as the frequency of the applied electric field increases. In particular, the ac conductivity of the transparent states in Fibonacci lattices, whose transmission coefficient is unity, shows a faster diminution in comparison with that of periodic systems. This fact is due to that in general these transparent states are isolated in the spectrum, *i.e.*, they are always surrounded by non transparent states, and the ac conductivity involves states within an interval of  $\hbar\omega$  around the Fermi energy. This work has been supported partially by CONACYT-32148E, DGAPA-IN105999, and UNAM-CRAY-SC008697.

SESSION K10/L6: JOINT SESSION  
QUASICRYSTAL  
Chair: Uwe Koester  
Wednesday Morning, November 29, 2000  
Room 200 (Hynes)

#### **8:30 AM \*K10.1/L6.1**

**FORMATION OF NANO ICOSAHEDRAL QUASICRYSTALLINE PHASE IN Zr-BASED BINARY AND TERNARY GLASSY ALLOYS.** Junji Saida, Mitsuhide Matsushita, Inoue Superliquid Glass Project, ERATO, Japan Science and Technology Corporation (JST), Sendai, JAPAN; Akihisa Inoue, Institute for Materials Research, Tohoku University, Sendai, JAPAN.

Since the reproducible formation of an icosahedral quasicrystalline phase as a primary precipitation phase from an amorphous state has been discovered in the Zr-Al-Ni-Cu-Ag alloy, the correlation between the icosahedral phase and a short-range ordering in the glassy state has attracted much attention in the aspects of the high glass-forming ability. The effect of constitutional elements on the formation of the icosahedral phase is also of importance in relation with the atomic configurations in the glassy state. Recently, we have found that a nano icosahedral phase in the diameter below 50 nm is formed as a primary phase in the crystallization reaction of the Zr-Ni-M (M=Pd, Au or Pt) and Zr-TM-Pd (TM=Fe, Co, Ni or Cu) ternary glassy alloys. These results imply that the formation and/or stabilization of the icosahedral phase is attributed to the existence of two kinds of strong chemical pairs of Zr-M and Zr-TM. Very recently, we have also found that a nano icosahedral phase is formed even in the Zr-(Pd and

Pt) binary alloys. It indicates that the dominant factor for the formation of the icosahedral phase is Zr-M pair. These results also suggest that an icosahedral short-range ordering exists in the Zr-(Pd or Pt) alloys. In this paper, we intend to present the transformation behavior of the nano icosahedral phase from the glassy state in the Zr-based binary and ternary glassy alloys.

#### **9:00 AM K10.2/L6.2**

**QUASICRYSTALS AND NANO-QUASICRYSTALS IN ANNEALED Zr-Al-Ni-Cu-Ag BULK METALLIC GLASSES.** M.W. Chen, I. Dutta, Naval Postgraduate School, Dept of Mechanical Engineering, Monterey, CA; A. Inoue, T. Sakurai, Tohoku University, Institute for Materials Research, Sendai, JAPAN.

Quasicrystals and nano-quasicrystals were discovered in annealed Zr-Al-Ni-Cu-Ag bulk metallic glasses by systematic transmission electron microscopic analysis. Selected area electron diffraction and micro-beam diffraction patterns corresponding to five-, three-, and two-fold rotational symmetry were obtained, demonstrating that the precipitated phases in the primarily devitrified bulk metallic glasses are icosahedral quasicrystalline phases. The formation of nano-quasicrystals is attributed to the high nucleation density. Moreover, the addition of Ag benefits the formation of the nano-quasicrystalline phase since energy-filtered elemental maps show that Ag slightly enriches into the nano-quasicrystals. The preliminary results of electron-energy-loss spectroscopy and phase transformation kinetics exhibit an interesting relationship between the bulk metallic glasses and the icosahedral quasicrystalline phases, which strongly supports that the local atomic structure is similar for the two solid states.

#### **9:15 AM \*K10.3/L6.3**

**NANOQUASICRYSTALLIZATION OF Zr-BASE METALLIC GLASSES.** B.S. Murty, D.H. Ping and K. Hono, National Research Institute for Metals, Tsukuba, JAPAN.

Recent investigations revealed that nanoquasicrystallization occurs in a number of Zr based metallic glasses. This paper reports our recent studies on the influence of various elements in the icosahedral phase formation in Zr-based metallic glasses for the purpose of understanding the essential conditions for nanoquasicrystallization. Icosahedral phase is formed in the first stage of crystallization reaction of the  $Zr_{65-x}Cu_{27.5}Al_{7.5}O_x$  amorphous alloys beyond a critical oxygen level, suggesting that oxygen is a factor to stabilize icosahedral phase formation in Zr-Cu(-Ni)-Al based metallic glasses. 3DAP results have clearly shown that oxygen is enriched in the icosahedral phase. On the other hand, Zr-based alloys containing Pd do not require oxygen for icosahedral phase formation. In the presence of Pd, even binary  $Zr_{100-x}Pd_x$  ( $x=30$  and  $35$ ) alloys show nanoquasicrystallization in the course of amorphous to crystal transformation. Based on 3DAP and TEM observation results together with kinetics analysis results, the quasicrystallization modes that occur during crystallization of Zr-based metallic glasses are discussed.

#### SESSION K11: SURFACES

Chair: Patricia Ann Thiel  
Wednesday Morning, November 29, 2000  
Room 203 (Hynes)

#### **10:00 AM K11.1**

**LOW-ENERGY ION SCATTERING MEASUREMENTS FROM AN Al-Pd-Mn QUASICRYSTAL.** Robert Bastasz, Josh Whaley, Sandia National Laboratories, Livermore, CA; Cynthia Jenks, Ames Laboratory and Dept of Chemistry, Iowa State University, Ames, IA; Thomas Lograsso, Ames Laboratory and Dept of Materials Science, Iowa State University, Ames, IA; and Amy Ross, Ames Laboratory, Ames, IA.

Energy-angle distributions of low-energy inert-gas ions scattered from surfaces provide a wealth of data about surface composition and structure. We have measured energy spectra of 500 eV  $He^+$  scattered from an  $Al_{0.72}Pd_{0.195}Mn_{0.085}$  quasicrystal, which was oriented perpendicular to the 5-fold axis, along various azimuthal directions. Strong scattering signals are seen from Al and Pd, but only a weak Mn signal is observed. From measurements made of  $He^+$  at an oblique angle of incidence ( $67.5^\circ$  from the sample normal) scattered in the forward direction ( $75^\circ$  laboratory scattering angle), we find a strong 5-fold periodicity in the azimuthal dependence of the scattering signals from Al and Pd surface atoms. The signal intensity variation arises from shadowing effects involving neighboring surface atoms. The data provide direct evidence that Al and Pd surface atoms in this quasicrystal exist in a local 5-fold symmetric environment. The domain size appears to be on the order of the width of the ion beam projected onto the surface. In addition, measuring the variation of the signal intensity at particular azimuthal orientations with incidence

angle provides information about nearest neighbor distances, which can be compared with models of the quasicrystal surface.

#### 10:15 AM \*K11.2

IRREVERSIBLE STRUCTURAL TRANSFORMATION OF FIVE FOLD i-Al-Pd-Mn QUASICRYSTALS AFTER ION BOMBARDMENT AND ANNEALING. Frank Schmithüsen<sup>1</sup>, Giovanni Cappello<sup>1,4</sup>, Sébastien Decossas<sup>1</sup>, Tien-Lin Lee<sup>1</sup>, Marc de Boissieu<sup>5</sup>, Yvonne Calvayrac<sup>6</sup>, Thomas Lograsso<sup>7</sup>, Joël Chevrier<sup>1,2,3</sup>, <sup>1</sup>ESRF, Grenoble Cedex, FRANCE; <sup>2</sup>LEPES-CNRS, Grenoble Cedex, FRANCE; <sup>3</sup>Université Joseph Fourier, Grenoble, FRANCE; <sup>4</sup>Laboratoire Physico-Chimie-Curie (PCC) UMR168, Institut Curie - Section de Recherche, Paris Cedex, FRANCE; <sup>5</sup>LTPCM INPG, Saint Martin d'Hères, FRANCE; <sup>6</sup>C.E.C.M.-C.N.R.S., Vitry Cedex, FRANCE; <sup>7</sup>Ames Laboratory/Iowa State University, Ames, IA.

Five fold i-AlPdMn surface prepared under UHV by ion bombardment and annealing was so far considered to be bulk terminated. This result was substantially based on a quantitative LEED analyses<sup>1</sup>. Analysis of the specular rod in a X ray diffraction experiment at grazing incidence supported this result<sup>2</sup>. We present a new study of this surface by high resolution X ray diffraction at normal incidence. In this Bragg configuration the diffraction peak (4222-2) is at a photon energy of 2.873keV. This results in an analyzed thickness of the sample surface of few  $\mu\text{m}$ .

The surface was cleaned by ion bombardment. During annealing ( $T=600^\circ\text{C}$ ), we observed the progressive disappearance of the initial Bragg peak characteristic of the as cast bulk sample. Conversely a new Bragg peak grows at an energy position shifted by 1eV compared to the position of the original Bragg peak. This is a clear signature for an irreversible structural transformation which takes place on at least the  $\mu\text{m}$  thickness. On the transformed surface, a RHEED pattern characteristic for a five fold surface was obtained.

This high resolution experiment (the relative Bragg peak shift is  $3 \times 10^{-4}$ ) was reproduced on samples from different origins. This shows that five fold i-AlPdMn surface changes after preparation by ion bombardment and annealing on a  $\mu\text{m}$  thickness. This is not consistent with the conclusion that the surface is simply terminated by a cut of the original bulk. This suggests that a reorganization process of the quasicrystalline structure during annealing starts at the surface and progresses towards the volume.

[1] M. Gierer et al., Phys. Rev. Lett. 78 (1997) 467

[2] J. Alvarez et al., Surf. Sci., 423 (1999) L251

#### 10:45 AM K11.3

QUASICRYSTALLINE SURFACES OF Al-Pd-Mn AND Al-Ni-Co: STRUCTURE AND USE AS NANOTEMPLATES. R. McGrath, J. Ledieu, E. Cox, Univ. of Liverpool, Surface Science Research Centre, Liverpool, UNITED KINGDOM; R.D. Diehl, Penn State University, Dept. of Physics, University Park, PA; D.W. Delaney, T.A. Lograsso, Iowa State Univ., Ames Lab., Ames, IA.

There has been substantial progress in relating the observed surface structure of AlPdMn to the known bulk structure; in contrast there is little information on the surface structure of AlNiCo. High contrast high resolution scanning tunnelling microscopy (STM) images of the 5-fold surface of AlPdMn obtained by altering tunnelling conditions provide new information on the surface structure and a new test for structural models. The ten-fold surface of AlNiCo has also been studied using Spot-Profile-Analysis Low Energy Electron Diffraction (SPA-LEED) and STM and the images reveal a flat surface without atomic resolution indicating a low surface corrugation. We have also considered the possibility of ordered adsorption on these surfaces. Of the several adsorbates we have investigated, the best candidate adsorbate is  $\text{C}_{60}$ . On the flat surface of AlPdMn,  $\text{C}_{60}$  molecules show one-dimensional correlations consistent with  $\tau$ -scaling but the expected 5-fold symmetry does not appear; this could be a result of the low density of molecules on the surface and the relatively large inter-molecular spacings. On the AlNiCo surface,  $\text{C}_{60}$  molecules form overlayers which do not appear to have symmetries related to the substrate. Prospects for further development of this area will be discussed.

#### 11:00 AM K11.4

TDS STUDY OF POTASSIUM ADSORPTION ON THE FIVEFOLD SURFACE OF AlPdMn. B.I. Wehner, C.J. Jenks, D.W. Delaney, T.A. Lograsso, A.R. Ross, P.A. Thiel, Ames Laboratory, Iowa State University, Ames, IA.

Thermal desorption spectroscopy in combination with AES is used to probe differences between the fivefold surface of AlPdMn, the metastable cubic overlayer on AlPdMn and Al(111). The Langmuir-Gurney model for alkali adsorption predicts a partial transfer of charge from the alkali metal adatom to the metal substrate at very low coverages and subsequent depolarization of these adatoms due to their mutual interaction as the coverage is increased. Using TDS, the decrease in desorption energy due to the depolarization of

the adatoms is studied. The interaction between the alkali adatom and the surface electronic structure is used to probe differences in the surface electronic structure.

#### 11:15 AM K11.5

EPITAXIAL METAL FILMS ON A DECAGONAL  $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$  QUASICRYSTAL. Masahiko Shimoda, Taku J. Sato, An Pang Tsai, National Research Institute for Metals, Tsukuba, JAPAN; Jun Quing Guo, CREST, Japan Science and Technology Corporation, JAPAN.

We performed metal depositions on the surface of quasicrystals with an aim of fabricating quasicrystals of simple substances. As a substrate, we chose the decagonal Al-Ni-Co quasicrystal with the tenfold surface, i.e. the surface exposing the quasiperiodic plane perpendicular to the tenfold axis. As already reported, the tenfold surface has the same quasiperiodic structure as in the bulk [1]. In the case of Au-depositions, an Au-Al alloy is formed instead of quasicrystalline Au. Reflection high-energy electron diffraction (RHEED) and X-ray photoelectron diffraction (XPD) measurements revealed that the alloy had no orientational order at room temperature. As a result of annealing, however, the surface turned to an epitaxial layer of multiply-twinned  $\text{AuAl}_2$  crystals with (110)-oriented surfaces and azimuthal orientations corresponding to the tenfold symmetry of the substrate. Thus we have succeeded for the first time in growing an epitaxial metal film on a quasicrystal.

[1] M. Shimoda, J.Q. Guo, T.J. Sato and A.-P. Tsai, Surf. Sci. 454-456 (2000) 11.

#### 11:30 AM \*K11.6

FACTORS AFFECTING THE STRUCTURE AND COMPOSITION OF CLEAVAGE SURFACES OF QUASICRYSTALS. Ph. Ebert, Institut fuer Festkoerperforschung, Forschungszentrum Juelich, Juelich, GERMANY.

The preparation of clean quasiperiodic surfaces is a challenging and delicate task due to changes in composition and structure of the well ordered intermetallic alloys during the conventional cleaning procedures by sputter and annealing cycles. Cleavage of quasicrystals allowed to avoid these changes and the resulting surfaces reflect the cluster-based bulk structure and the atom columns of the icosahedral and decagonal quasicrystals, respectively. However, measurements after heat treatment suggested that the cluster-based structure of the cleavage surfaces is thermally unstable, since in some areas considerable changes in composition and structure were observed. Here we demonstrate that cleavage surfaces of Al-Pd-Mn quasicrystals are rather thermally stable. A supersaturation of bulk vacancies is found to be responsible for the changes in composition and structure at the surfaces. If the samples are suitably annealed to remove the supersaturation of vacancies no changes of the surfaces are observed. We illustrate that these effects can be used to characterize the homogeneity of vacancies in intermetallic alloys using the examples of Al-Pd-Mn and Al-Ni-Co quasicrystals. We will also discuss the effects of oxygen and other contaminations on the structure and composition of cleaved quasicrystal surfaces and how they affect investigations of the surface structure. This work has been done in collaboration with F. Kluge, B. Grushko, T. Cai, P.A. Thiel, and K. Urban.

#### SESSION K12: ELECTRONIC STRUCTURE

Chair: Uichiro Mizutani

Wednesday Afternoon, November 29, 2000

Room 203 (Hynes)

#### 1:30 PM \*K12.1

BAND STRUCTURE AND ELECTRON TRANSPORT IN Zn-Mg-Y SYSTEM. Y. Ishii, Chuo Univ, Dept of Physics, Tokyo, JAPAN; T. Fujiwara, Univ of Tokyo, Dept of Applied Physics, Tokyo, JAPAN.

Zn-Mg-R (R=rare earth) alloys form a series of unique hexagonal crystals (approximants) in a composition range close to icosahedral quasicrystals. We have studied electronic structure of the hexagonal Zn-Mg-Y alloy to understand mechanism of stability and physical properties of the icosahedral phase. It is found that a pseudo-gap at the Fermi level is clearly seen in the electronic density of states for the hexagonal phase with a lattice parameter  $a = 1.46 \text{ nm}$ . Such distinct pseudo-gap has never been obtained in the electronic states of the approximant crystals without transition metals, including  $\text{Mg}_{32}(\text{Al}, \text{Zn})_{48}$  Bergman phase and  $\text{Zn}_2\text{Mg}$  hexagonal Laves (C14) phase. Localization of the valence electron density is found between Zn atoms at particular sites and it is confirmed that such Zn-atoms pair is responsible for the pseudo-gap formation. We shall discuss possible effects of the Zn-Zn bond on the transport properties of this system.

#### 2:00 PM \*K12.2

ELECTRONIC STRUCTURE AND TRANSPORT PROPERTIES OF ICOSAHEDRAL AND DECAGONAL QUASICRYSTALS.

Jürgen Hafner<sup>a</sup> and Marian Krajčí<sup>a,b</sup>, <sup>a</sup>Institut für Materialphysik and Center for Computational Materials Science, Universität Wien, AUSTRIA; <sup>b</sup>Institute of Physics, Slovak Academy of Sciences, Bratislava, SLOVAKIA.

First-principles calculations of the electronic structure and transport properties of icosahedral and decagonal quasicrystals are reviewed. It is shown that in icosahedral quasicrystals for which the electronic density of states at the Fermi level is dominated by s,p-electrons (Al-Zn-Mg, Al-Cu-Li,...), the existence of a structure-induced pseudogap may contribute to the stability of the quasicrystalline phase. On the other hand, the pseudogap in the Al-s,p band may be almost completely covered by the d-band of a transition-metal component with an incompletely filled band (Al-Pd-Mn, Al-Pd-Re,...). In this case, both calculations and spectroscopic evidence agree on the important role of covalent d-d interactions. d-d hybridization is also of decisive importance in determining the stability and the local chemical order of decagonal quasicrystals (Al-Pd-Mn, Al-Cu-Co, Al-Ni-Co). Spin-polarized calculations are used to discuss the conditions for the formation of magnetic moments in both icosahedral (Al-Pd-Mn, Gd-Zn-Mg) and decagonal (Al-Pd-Mn) quasicrystals. Calculations of the electronic transport properties using both the Boltzmann- and Kubo-Greenwood formalisms are presented.

#### 2:30 PM \*K12.3

VALENCE BAND STRUCTURE OF QUASICRYSTALS STUDIED BY PHOTOEMISSION: OBSERVATION OF DISPERSING STATES. Eli Rotenberg, Advanced Light Source, Lawrence Berkeley Lab, Berkeley, CA; Wolfgang Theis, Fachbereich Physik der Freien Universität Berlin, GERMANY; Karsten Horn, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, GERMANY; Peter Gille, Institut für Kristallographie und Angewandte Mineralogie der Ludwig-Maximilians-Universität München, GERMANY.

Quasicrystals possess perfect long-range structural order in spite of the fact that their rotational symmetries are incompatible with long-range periodicity. The question whether the unusual physical properties of quasicrystals are a consequence of these exotic structural properties is largely unresolved, since an interpretation of valence electron state nature, in terms of either extended (as in periodic crystals) or localized states (as in amorphous materials), is still missing. To address this question, we have directly measured the momentum (*k*-) dependent distribution of the electronic states in d-AlNiCo using high-resolution, *k*-resolved photoemission measurements at the Advanced Light Source in Berkeley, CA. The photoemission data show that the valence electrons feel the symmetry of the quasicrystalline structure, since angular intensity maps provide clear evidence for a tenfold or twofold (AlNiCo) rotationally symmetric emission pattern. Valence band spectra show peaks that disperse continuously with wave vector, in the directions normal and parallel to the sample surface. The dispersions are found to be periodic (as expected) along the periodic, 10-fold axis, and aperiodically distributed in the aperiodic, 10-fold plane. The effective mass of some of these states approaches  $\{m^* = 1\}$ , indicating a high degree of delocalization. We present renderings of the constant energy surfaces in momentum (*k*-) space, and find that the s-p bands have spherical energy surfaces emanating from the locations of the strongest in-plane diffraction spots, supporting a picture in which the strongest Fourier components of the atomic potential define a pseudo-Brillouin zone. We also find d-derived states of both localized and delocalized character crossing the Fermi level, and thus forming a well-defined Fermi surface. Considering that the response function of the electrons derives from the detailed topology of the Fermi surface, these results should have a bearing on many of the electronic properties of decagonal AlNiCo in particular and quasicrystals in general.

#### SESSION K13: TRANSPORT PROPERTIES

Chair: Esther Belin-Ferre  
Wednesday Afternoon, November 29, 2000  
Room 203 (Hynes)

#### 3:30 PM \*K13.1

DETERMINATION OF SPATIALLY HYBRIDIZED CHARGE DISTRIBUTION AND ITS EFFECT ON ELECTRON TRANSPORT IN THE Al-Cu-Ru-Si 1/1-APPROXIMANT. U. Mizutani, T. Takeuchi, E. Banno, V. Fournée, Nagoya Univ, Department of Crystalline Materials Science, Nagoya, JAPAN; M. Takata, M. Sakata, Department of Applied Physics, Nagoya Univ, Nagoya, JAPAN; H. Sato, Aichi Univ. of Education, Aichi-ken, JAPAN.

A single-phase Al<sub>68</sub>Cu<sub>7.3</sub>Ru<sub>16.7</sub>Si<sub>8</sub> 1/1-approximant was synthesized by annealing arc-melted ingot at 680°C for 12 hr. Its space group is found to be Im $\bar{3}$ . Positions of 144 atoms in the unit cell and the charge distribution were determined by the Maximum Entropy

Method combined with Rietveld analysis (MEM/Rietveld analysis) using synchrotron powder diffraction data measured at BL02B2 in SPring-8. The valence band structure was calculated in the framework of the TB-LMTO method by approximating the experimentally derived atomic structure to the one permissible to the band calculations. Here the existing chemical disorder in clusters has to be ignored. The validity of the present band calculations was checked by comparing the calculated valence band structure with measured photoemission spectra. Encouraged with this agreement, we calculated the charge distribution in the real space by using the eigenfunctions for different energy eigenvalues. The present band calculations coupled with DV-X $\alpha$  cluster calculations revealed that the bonding state is formed a few eV below the Fermi level due to hybridization effect between the neighboring Ru-4d and Al-3p states and also between Cu-3d and Al-3p states. The depletion of electrons at the Fermi level due to the hybridization effect above is well reflected in the charge distribution map for electrons at the Fermi level. The reason for the possession of a relatively high resistivity of 690  $\mu\Omega$ -cm of this approximant can be discussed on the basis of the resulting hybridized charge distributions for electrons at the Fermi level and for those at binding energies where the formation of bonding state is significant.

#### 4:00 PM \*K13.2

ABOUT THE METAL-INSULATOR TRANSITION IN QUASICRYSTALS. J. Delahaye, C. Berger, T. Schaub, T. Grenet, Laboratoire d' Etude des Propriétés Electroniques des Solides, CNRS, Grenoble, FRANCE; J.P. Brison, J.J. Préjean, Centre de Recherches sur les Très Basses Températures, CNRS, Grenoble, FRANCE.

Electronic properties of quasicrystals are presented in the light of the current theories of Mott-Anderson for the zero-temperature metal-insulator (MI) transition. This outlines the role of electron-electron interaction and disorder in quasicrystals. On the metallic side of the transition, we revisit the conductivity of the i-AlPdMn single grains and I-AlCuFe thin films samples. We show strong similarities for the electrical conductivity and density of states measurements between the AlPdRe icosahedral phase and various systems where the MI transition was identified such as Si:B or inOx for instance. In i-AlPdRe, the electrical conductivity and its correlated temperature dependence spread over a wide range ( $\sigma_{4K}$  from  $\sim 1 \Omega^{-1}\text{cm}^{-1}$  to  $10^2 \Omega^{-1}\text{cm}^{-1}$  and  $R = \sigma_{4K}/\sigma_{300K}$  from 220 to 2, respectively), on both sides of the MI transition. At high temperature, power law temperature dependences are observed, whereas differences develop in the conductivity at low temperatures depending on the insulating nature or not of the samples. In particular, in the more resistive samples, the metallic-like plateau around 1K is followed by a sharp drop of the conductivity as temperature is decreased down to 20mK which is our lowest reachable temperature for confident sample cooling. The whole temperature dependence of the conductivity for samples of different electrical behavior can be explained within the framework of the Mott-Anderson MI transition. Finally, electronic density of states measurements (specific heat, tunneling spectroscopy and photoemission spectroscopy) are also in agreement with this conductivity analysis. The single square root energy dip found in the spectroscopic data is interpreted by inter-electronic interactions like in doped semiconductor systems.

#### 4:30 PM K13.3

ELECTRICAL RESISTIVITY OF AN Al-Re-Si CUBIC APPROXIMANT PHASE. Ryuji Tamura, Takayuki Asao, Mutsuhiro Tamura, Shin Takeuchi, Science Univ of Tokyo, Dept of Materials Science and Technology, Chiba, JAPAN.

The role of d-orbitals on the electronic transport of the i-phase is supposed to be of significance, since very high resistivity and its strong temperature variation have been observed only in i-phases containing transition metal (TM) atoms, such as i-AlCuTM (TM=Fe,Ru,Os) and i-AlPdTM (TM=Mn,Re). From this aspect, the electronic transport of Al-Re-Si 1/1-approximant phase is of great interest since it contains the same Re atom as i-AlPdRe, where the d-orbitals of Re atoms are supposed to be partly responsible for the insulating behavior, and strong resonance due to the Re d-orbital is thus expected.  $\alpha$ -AlReSi of various compositions typically around Al<sub>73</sub>Re<sub>15</sub>Si<sub>12</sub> was prepared by arc-melting. The phase has been characterized by means of x-ray diffraction and electron diffraction measurements. The electrical resistivity was measured for samples of various Re concentrations by the four probe method in the range between 12 K and 300 K. The highest resistivity and the highest resistivity ratio ( $\rho_{12K}/\rho_{300K}$ ) have been observed at 17.4 at.%Re. When the Re concentration is reduced, both the resistivity and resistivity ratio substantially decrease. The sensitiveness of the resistivity to the Re concentration, or to the substitution of Al and Si atoms in the TM clusters, indicates that the icosahedral clusters exclusively made of Re atoms have a strong influence upon resonance between d- and sp-orbitals near  $E_F$ . The same situation may also occur in case of the i-phase.

**4:45 PM K13.4**

CLASSIFICATION OF ICOSAHEDRAL QUASICRYSTALS AND THEIR APPROXIMANTS BY THE ELECTRONIC TRANSPORT MECHANISM. Tsunehiro Takeuchi, Eiichi Banno, Tomohide Onogi, Takayuki Mizuno, Takuya Sato, Fournée Vincent and Uichiro Mizutani, Department of Crystalline Materials Science, Nagoya University, JAPAN.

In the present study, we treat the quasicrystals (QC's) and approximants (AC's) as being in a class of the disordered system without considering any special transport mechanism specific to the quasiperiodicity. Here, two independent effects should be separated to explain resistivity behavior of all kinds of QC's and AC's systematically. One is the effect due to the electronic structure at  $E_F$  and the other is the scattering effect due to the disorder in the atomic structure. We plot resistivities at 4K and 300K ( $\rho_{4K}$  and  $\rho_{300K}$ ) as functions of residual resistivity ratio ( $RRR = \rho_{4K}/\rho_{300K}$ ) for a number of QC's and AC's. In this plot, the QC's and AC's are successfully classified into three groups. The first group can be well described in terms of the Boltzmann transport equation (BTE), in which relaxation time ( $\tau$ ), area of Fermi surface ( $S_F$ ) and Fermi velocity ( $v_F$ ) play dominant roles. The second group, which appears at  $RRR \geq 1.2$ , is characterized by the Mott's  $g^2$ -factor and the weak localization (WL). Here, only  $S_F$  contributes through the Mott's  $g^2$ -factor, but the others,  $\tau$  and  $v_F$ , have no longer meaningful role. The third group is in the vicinity of metal-insulator transition, in which the WL theory breaks down. Variable range hopping conduction observable in the third group suggests that the Anderson localization takes place. Among the key words listed above,  $S_F$ ,  $v_F$  and Mott's  $g^2$ -factor are the parameters which represent the effects of the electronic structure at  $E_F$ . On the other hand, the scattering due to the disorder makes  $\tau$  in the first group shorter. When the scattering becomes stronger, the WL takes place, and much stronger scattering leads a complete localization of electrons.

## SESSION K14: MAGNETISM - THERMOELECTRIC

Chair: Yasushi Ishii  
Thursday Morning, November 30, 2000  
Room 203 (Hynes)

**8:30 AM \*K14.1**

SPIN DYNAMICS IN THE ICOSAHEDRAL Zn-Mg-RE (RE=RARE EARTH) QUASICRYSTALS. Taku J. Sato, Hiroyuki Takakura, An Pang Tsai, NRIM and CREST-JST, Tsukuba, JAPAN; Hiroaki Kadowaki, Tokyo Metropolitan Univ, Dept of Physics, Tokyo, JAPAN; Kaoru Shibata, Tohoku Univ, IMR, Sendai, JAPAN.

Magnetic susceptibility of the Zn-Mg-RE (RE: rare-earth) quasicrystals shows typical spin-glass-like behavior [1]. Recently, however, we observed significant static short-range spin correlations that were described by a six-dimensional (6D) modulation vector [2]. Since the 6D correlations are essentially related to the quasiperiodicity, spin ordering in the quasicrystals may differ from that in ordinary spin glasses. To elucidate the difference, we have measured spin dynamics in the Zn-Mg-Tb quasicrystal using neutron-inelastic-scattering, ac-susceptibility and dc-magnetization-relaxation techniques. From those results, characteristic relaxation time was evaluated for the time scale of  $10^{-12}$  s to  $10^4$  s. We found that temperature dependence of the relaxation time does not obey the power law. Thus, the quasicrystal has presumably no finite-temperature spin-glass phase transition. In addition, the neutron scattering spectrum shows strong (possibly-) quasielastic scattering; it has a spectral width of about 2 meV at  $T \simeq 1.5$  K, and is almost Q-independent. This suggests possible existence of spatially-localized spin fluctuations with an anomalously large energy scale even at the lowest temperature. These results are in stark contrast to three-dimensional spin glasses. [1] Y. Hattori et al., J. Phys. Condens. Matter 7 (1995) 2313. [2] T.J. Sato et al., Phys. Rev. Lett 81 (1998) 2364; T.J. Sato et al., Phys. Rev. B61 (2000) 476.

**9:00 AM \*K14.2**

ORIGIN OF MAGNETISM IN Al-Pd-Mn AND Al(Si)-Mn QUASICRYSTALS AND APPROXIMANTS. Virginie Simonet, Françoise Hippert, Laboratoire de Physique des Solides, Univ Paris-Sud, Orsay, FRANCE; Marc Audier, LMGP, ENSPG, Saint Martin d'Heres, FRANCE; Yvonne Calvayrac, CECM, Vitry, FRANCE; Robert Bellissent, Laboratoire Léon Brillouin, CEN Saclay, FRANCE; Guy Trambly de Laissardière, Laboratoire de Physique Théorique et Modélisation, Univ de Cergy-Pontoise, FRANCE; Didier Mayou, Laboratoire d'Etude des Propriétés Electroniques des Solides, Grenoble, FRANCE.

Whereas most quasicrystals are diamagnetic, localised moments are observed on a small fraction of the Mn atoms in Al-Pd-Mn and

Al(Si)-Mn quasicrystals. In contrast, a large proportion of magnetic moments is found in liquids in equilibrium with these quasicrystalline phases. In quasicrystals, no identification of the magnetic sites could be performed, because of the very low number of Mn atoms involved and the incomplete knowledge of the atomic structure. The origin of magnetism remained therefore unclear. Thus we have undertaken the study of crystalline approximant phases in the Al(Si)-Mn and Al-Pd-Mn systems. Although most of them are non-magnetic, we found three exceptions, the  $\mu$  Al<sub>4</sub>Mn phase, the Mn-rich Taylor phase and the 1/1 Al-Pd-Mn-Si approximant. By combining experimental and theoretical investigations, we have identified the magnetic sites in these phases. The moment formation cannot be explained by the effect of the local environment of the Mn atoms only. Indirect Mn-Mn interactions on a relatively large distance (5 Å and more) mediated by the conduction electrons also play an important role. A clear picture of the origin of magnetism in quasicrystals, approximants and liquids in the Al-Mn and Al-Pd-Mn systems can be obtained from these results.

**9:30 AM K14.3**

ELECTRON TRANSPORT PROPERTIES AND THERMOELECTRIC EFFECT OF Al-Pd-Mn SINGLE QUASICRYSTALS DOPED WITH M=Au OR Re BY ION IMPLANTATION AND ITS COMPARISON WITH QUATERNARY QUASICRYSTALLINE SAMPLES. V. Fournée<sup>a</sup>, U. Mizutani<sup>a</sup>, T. Takeuchi<sup>a</sup>, H. Saitoh<sup>b</sup>, M. Ikeyama<sup>b</sup>, J.Q. Guo<sup>c</sup>, A.P. Tsai<sup>c</sup>; <sup>a</sup>Department of Crystalline Materials Science, Nagoya University, JAPAN; <sup>b</sup>National Industrial Research Institute of Nagoya, Nagoya, JAPAN; <sup>c</sup>National Research Institute for Metals, Tsukuba, JAPAN.

A single grain icosahedral quasicrystal  $i$ -Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> was produced by using the floating zone technique. The growth direction is parallel to the 2 fold axis. Several rectangular samples were cut from this button, with an approximate size of  $8 \times 2.5 \times 0.5$  mm<sup>3</sup>, and oriented along the three different symmetry axes. The temperature dependencies of the electrical resistivity and thermopower were measured and didn't show any significant orientation dependence. Then we performed ionic implantation in these samples, either with Au or Re atoms, using various fluences. The concentration profile of the implanted elements were analysed by RBS spectroscopy, as a function of depth below the implanted surface. The maximum of the distribution is located at about 0.3  $\mu$ m below the surface. To increase the ratio of the implanted layer thickness to that of the bulk QC, we reduced the total thickness of the sample down to 50  $\mu$ m. The measured resistivity and thermopower are reduced as compared to non-implanted samples, which is likely due to the presence of the strongly disordered layer resulting from high-energy ionic implantation. In order to restore the structural order in this layer, the samples were annealed at 500°C for 30 min. The resistivity values almost recover those measured for non-implanted samples, suggesting that the quasiperiodic order has been restored. In the case of Au-implanted samples, the thermopower is further reduced after annealing, whereas a significant increase above the non-implanted values is measured in the case of Re-doped samples. Those are encouraging results in the prospect of quasicrystals as possible thermoelectric materials. We will compare the effect of Re atoms on the electron transport properties introduced by ionic implantation in a single grain  $i$ -Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5</sub> to quaternary  $i$ -Al<sub>72</sub>Pd<sub>19.5</sub>Mn<sub>8.5-x</sub>Re<sub>x</sub> alloys obtained by usual metallurgical techniques.

**9:45 AM K14.4**

THERMOPOWER IN QUASICRYSTALLINE SYSTEMS. A.L. Pope, R. Schneidmiller, T.M. Tritt, J. Kolis Clemson University, Clemson, SC; R. Gagnon, J. Strom-Olsen, S. Legault McGill University, CANADA.

We report thermopower values for several quasicrystalline systems: AlPdMn, AlPdRe, and AlCuFe. Striking differences are observed in the conduction mechanisms between the quasicrystalline families. Thermopower is observed to be as large as 80  $\mu$ V/K. Variable range hopping is observed to govern low temperature thermopower in AlPdMn and AlPdRe quasicrystals. In an effort to further understand the complexities of electrical transport in quasicrystalline systems, thermopower data for icosahedral Al<sub>71</sub>Pd<sub>21</sub>Mn<sub>8-x</sub>Re<sub>x</sub> will be presented. In addition, the effects of the addition of a fourth element to a base quasicrystalline system will be discussed.

## SESSION K15: APPLICATIONS

Chair: Shin Takeuchi  
Thursday Morning, November 30, 2000  
Room 203 (Hynes)

**10:30 AM \*K15.1**

BEYOND THE USEFULNESS OF QUASICRYSTALS. Jean-Marie Dubois, CNRS, Ecole des Mines, Nancy, FRANCE.

For a decade, quasicrystals were considered to exhibit only fundamental interest in so far that they raised basic questions regarding the organization and stability of condensed matter. As well, they addressed the mechanisms of wave propagation in aperiodic solids. In more recent years, they turned to become useful materials in various mechanical devices, in solar absorbers or in heat insulation coatings. The talk will review the state of this art. More emphasis will be put on the new subjects that the supposedly useful quasicrystals have forced us to study rather than on the few possible breakthroughs of quasicrystalline materials identified yet on the market. Tribology and wetting by polar liquids are such examples in which studies of series of quasicrystals and their approximants allows to tune finely the metallic character of the sample surface. Processing of thin quasicrystalline films is another example from which new ideas emerge regarding the nucleation of metastable phases.

**11:00 AM \*K15.2**

**POSSIBLE INDUSTRIAL APPLICATIONS OF Al-BASED QUASICRYSTALS: PLASMA THERMAL SPRAYING VS. HVOF.** Do Hyang Kim, Eric Fleury, Jae Soo Kim, Yu Chan Kim, Won Tae Kim, Sang Mok Lee, Yonsei Univ. Center for Noncrystalline Materials, Seoul, KOREA.

Possibility of utilizing the fascinating properties of Al-based quasicrystals were widely examined by employing the two representative thermal spraying methods - plasma thermal spraying and HVOF (high velocity oxygen fuel) techniques. Al-Cu-Fe-X(B) (X= Be, Si, and Cr) and Al-Ni-Co(B) systems were applied to both techniques to produce quasicrystalline phase containing coating layer onto the SUS304 substrate. The forming ability of the quasicrystalline phase and phase equilibria of the deposited coating layer were investigated as functions of processing parameters. Various processing parameters were found to exert significant effects on the microstructural evolution and subsequent mechanical/physical properties of the coating layers produced by the two techniques. The coating characteristics of various Al-based quasicrystal systems, such as, phase constitution, porosity level, hardness, bonding strength, surface property, were compared between the plasma spraying and HVOF coating layers. Tribological characteristics were also evaluated under various testing conditions using a classical pin-on-plate experimental device. Friction and wear behaviors of the coating layer were discussed based on friction measurements and various analytical techniques including XPS, Auger spectroscopy, and AFM.

**11:30 AM \*K15.3**

**QUASICRYSTALLINE COATINGS THROUGH LASER PROCESSING: A STUDY ON PROCESS OPTIMISATION AND MICROSTRUCTURE EVOLUTION.** K. Chattopadhyay<sup>1</sup>, K. Biswas<sup>1</sup>, G. Phanikumar<sup>1</sup>, S. Bysakh<sup>1</sup>, A. Weisheit<sup>2</sup>, B.L Mordike<sup>2</sup>; <sup>1</sup>Department of Metallurgy, Indian Institute of Science, Bangalore, INDIA; <sup>2</sup>Technical University, Clausthal, GERMANY.

The present talk deals with the efforts to obtain quasicrystalline coatings of Al-Cu-Fe alloys through laser processing using elemental powders. Two substrates of Al and Al-Si alloy were used. A two step process of first laser cladding followed by laser remelting to fine tune solidification parameter has been adopted. The cladding was carried out at two different velocities (300 and 600 mm/min). The remelting was done at velocities ranging from 300 to 1500 mm/min. The composition of the Al-Cu-Fe powder mixture is found to be the most important variable in the formation of I-phase in the clad pool. The base powder mixture composition  $Al_{63}Cu_{20}Fe_{15}$  with Cu/Fe = 2/1 is found to be optimal for formation of I-phase. XRD analysis showed the presence of I-phase along with  $(Al,Cu)_{13}Fe_4(\lambda)$ ,  $CuAl_2$  and occasional decagonal phase. Remelting increases the I-phase content. The I-phase content increases in the pools on Al-Si substrates due to presence of Si. SEM analysis showed the presence of I-phase in the interdendritic regions of  $CuAl_2$ . TEM analysis depicted the presence of  $\lambda$  along with I-phase with orientational relationship  $[010]_{\lambda} \parallel [000001]_I$ . A detailed analysis of the solidification pathway for quasicrystal formation and the development of associated crystalline phases through laser processing route will be presented and compared with other processing routes.

SESSION K16: APPLICATIONS (continued)

Chair: Jean-Marie Dubois  
Thursday Afternoon, November 30, 2000  
Room 203 (Hynes)

**1:30 PM K16.1**

**QUASICRYSTALLINE MATERIALS FOR THERMOELECTRIC APPLICATIONS.** T.M. Tritt, A.L. Pope, R. Schneidmiller, J. Kolis, Clemson University, Clemson, SC; R. Gagnon, J. Strom-Olsen, S. Legault, McGill University, CANADA.

With inherently low thermal conductivity and promising electrical transport properties, quasicrystals are being investigated for their potential as thermoelectrics to be utilized for power generation. In order to determine a quasicrystals viability as a thermoelectric material, extensive thermal and electrical transport measurements must be performed on the same sample. This is due in large part to the variability in transport properties from sample to sample. In this paper, the interplay between thermopower and resistivity will be discussed as well as the electronic contribution to thermal conductivity. Also presented will be the current theoretical predictions for the potential of these materials as thermoelectrics and its agreement for the best quasicrystalline thermoelectric material to date.

**1:45 PM K16.2**

Abstract Withdrawn.

**2:00 PM \*K16.3**

**HIGH PERFORMANCE QUASICRYSTAL-REINFORCED POLYMER COMPOSITES.** Valerie V. Sheares, Paul Bloom, K.G. Baikerakar, Iowa State University, Dept. of Chemistry, Ames, IA.

The tailoring of materials to give a desired set of properties is often accomplished synthetically with the production of a new polymer. However, a less expensive alternative is the addition of fillers to existing materials. As this field becomes more advanced, there is an expanded search for additives which address more sophisticated enhancement of electrical and chemical resistance, surface properties, etc. To this end, the Sheares group has fabricated new high temperature polymer/quasicrystal composites. The properties of the quasicrystal additives, low thermal conductivity, low coefficients of friction and high hardness, make them ideal materials to evaluate in polymer composites. The high performance polymers chosen are processable with softening temperatures less than 500°C and are thermally stable from 400-600°C. The combination of both materials in a composite should improve the processability of the quasicrystals, while enhancing the performance of the polymers. The group has demonstrated that the quasicrystals will uniformly disperse in a polymer matrix, will not adversely affect the thermal properties and will improve the mechanical properties of the polymer, much like other hard fillers. However, it is the properties that are unique to the quasicrystal/polymer combination that are generating industrial interest. For example, the wear properties of the polymer/quasicrystal composite are significantly improved over the polymer alone. These properties are superior to other polymer/hard filler composites containing silicon carbide and aluminum oxide, presumably due to the low surface energy and high hardness of the quasicrystals. In fact, in spite of the high hardness of the quasicrystals, the counterface material is not eroded to the same extent as when other hard fillers are utilized. The excellent wear properties point to potential applications in low friction bearings, gears, etc. The fabrication, in addition to the thermal, mechanical, wear, and thermal conductivity properties of these unique materials, will be discussed.

**2:30 PM \*K16.4**

**QUASICRYSTALLINE CATALYST FOR STEAM REFORMING OF METHANOL.** Masatoshi Yoshimura, An Pang Tsai, Mitsubishi Gas Chemical Co. Corporate Res. Lab. Tsukuba, JAPAN; National Research Institute for Metals, Tsukuba, JAPAN.

The steam reforming of methanol has been performed on a stable AlCuFe icosahedral quasicrystal. The AlCuFe quasicrystal reveals excellent activity with the same level as that of industrial catalyst for steam reforming of methanol. The X-ray diffraction, transmission and scanning electron microscopy have been employed to understand the mechanism of the reactions on the quasicrystalline alloy. Details will be given in the talk.

**3:00 PM \*K16.5**

**INTERRELATION BETWEEN HUME-ROTHERY MECHANISM, HYBRIDIZATION AND COVALENT BONDS IN ALUMINUM- AND BORON-BASED ICOSAHEDRAL APPROXIMANTS AND QUASICRYSTALS.** Kaoru Kimura, Kazuhiro Kirihiro, Masaaki Fujimori, Takahiro Nakayama, Univ. of Tokyo, Dept of Advanced Materials Science, Tokyo, JAPAN; Masaki Takata, Makoto Sakata, Nagoya Univ., Dept of Applied Phys., Nagoya, JAPAN.

The origin of the pseudogap in Al-based icosahedral phases is considered to be due to a Fermi surface Jones zone (FS-JZ) interaction such as that exhibited in Hume-Rothery alloys; an interaction enhanced when the Fermi-sphere diameter  $2k_F$  matches the wave number of the intense Bragg peak  $K_p$ . By estimating  $2k_F$  from the valence electrons per atom ratio ( $e/a$ ), we found that  $2k_F$  in  $\alpha$ -AlMnSi is quite close to  $K_p$  of the intense (530) peak corresponding to the pseudo-five-fold direction. The Hume-Rothery picture, however, applies to a nearly free electron system in which the potential of the



valence electron is rather weak. In the case that  $2k_F$  is close to  $K_p$ , then one of two standing waves created from two plane waves is stabilized and occupied by the electron while the other is empty such that the electron density distribution becomes inhomogeneous and dense regions appear. The energy difference between two standing waves, the depth of the pseudogap, and the inhomogeneity of the electron density distribution increase with increasing potential. Accordingly, for a sufficiently deep pseudogap, it is easy to see dense regions of valence electrons as covalent bonds as in  $\beta$ -gallium, a metallic molecular crystal. Regarding  $\beta$ -AlMnSi, it is similar to that of  $\beta$ -gallium in that the origin of the pseudogap is considered to be due to the covalent bonds rather than the Hume-Rothery mechanism<sup>1</sup>. In the AlPdRe icosahedral phase, the enhancement of electrical resistivity with increasing concentration of transition metals is due to the enhanced covalency between Al and TM. Such hybridization-induced band gaps also exist in Al-Ru and Al-Fe alloys, with the real gap being formed at  $E_F$  in  $Al_2Ru$  intermetallic compounds. These systematic studies, including that of icosahedral boron-rich solids<sup>2</sup>, should lead us to a fundamental understanding, e.g. the relation between Hume-Rothery mechanism, hybridization and covalent bonding, in these unique icosahedral cluster-based solids.

<sup>1</sup> K. Kirihara et.al.: Phys. Rev. Lett. (2000) in press.

<sup>2</sup> M. Fujimori et.al.: Phys. Rev. Lett. 82, 4452 (1999).