SYMPOSIUM LL
LL: Quasicrystals

November 30 - December 3, 2003

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*Invited paper
TUTORIAL

PT LI: Quasicrystals: Relationships Between Surface and Bulk Phenomena
Sunday, November 30, 2003
100 PM - 5:00 PM
Room 201 (Hynes)

The tutorial will cover recent advances in the basic surface science of quasicrystals and the way that this new knowledge relates to our understanding of the bulk materials. Specific topics are: a) atomic and electronic structure; b) role and nature of vacancies; c) role of clusters; and d) orientational relationships at interfaces. The tutorial will begin with an introductory talk on the general tools and principles of surface science as they relate to the work that has been done in the field of quasicrystals, e.g., gas flux and exposure; the value of using complementary techniques; the definition of a surface vs. the bulk; qualitative analysis, and typical information depths for electrons vs. photons.

Instructors:
Patricia A. Thiel, Iowa State University
Romain McGrath, The University of Liverpool

SESSION LI: Synthesis and Structure I
Chairs: D. H. Kim and A. P. Tsai
Monday Morning, December 1, 2003
Fairfax A (Sheraton)

8:30 AM *LI.1.1
Search and synthesis of new family of quasicrystals.
Tsutomu Ishimasa, Graduate School of Engineering, Hokkaido Univ., Sapporo, Hokkaido, Japan.

Approximate crystals may be very important and useful to find new quasicrystal alloys. In the framework of the projection method, an approximate crystal can be understood as rational approximation of the corresponding quasicrystal. In the case of an icosahedral quasicrystal, an approximate includes a local atomic configuration or atomic cluster satisfying approximately the icosahedral symmetry. Bergman- and Mackay-type clusters are famous examples of atomic clusters. Recently, stimulated by the discovery of binary stable quasicrystals in Cd-Yb and Cd-Cu [1], a new type atomic cluster has been recognized, which we call here ‘Thie-type’ cluster. Common characteristics of this cluster is triple shells: in the case of cubic Zn17Sc3 approximate, for example, the cluster consists of the innermost icosahedral shell of 20 Zn, the icosahedral shell of 25 Sc and the outermost icosidodecahedral shell of 30 Zn [2]. Thie-type cluster can be found in variety of alloys, namely Be-, Co-, Zn-, Ga-, Al- and In-based alloys. Accordingly, there is a lot of possibility to find new quasicrystalline alloys with different base metals. In the present work, the Zn17Sc3 crystal was selected as a starting approximate. By replacing 5 at. % Zn with Mg, a 3D icosahedral quasicrystal was found at the alloy composition of Zn80Mg5Sc15 [3]. This quasicrystal is thermodynamically stable and has very high structural quality. Millimeter-sized single grains of the quasicrystal are formed by slow cooling from the melt. Furthermore, it is possible to replace Zn with Cu and Sn, which are two neighbors of Zn in the periodic table. The Cu0.80Sn0.20Mg0.38Sc0.15 quasicrystal is also thermodynamically stable. Substituting Ti for Sc, Zn8Mg(0.17)Sc1 was obtained. It is also possible to replace Sc with Yb. In this case Zn7Mg(0.14)Sc1 is formed. The latter two quasicrystals are considered to be metastable. These new quasicrystals have almost the same average valence electron concentration, e/a, ranging from 2.00 to 2.16. This fact indicates important role of Hume-Rothery mechanism for the stabilization of these quasicrystals. [1] A. P. Tsai, J. Q. Guo, E. Abe, H. Tsuchiya and T. J. Schultz, Nature 418 (2002) 517. [2] K. Andrayan, B. YA. Kotur and V. E. Zvonik, Kristallografiya 34 (1989) 996. [3] Y. Kano, Y. A. Arakcheeva and T. Ishimasa, Phil. Mag. Lett. 81 (2001) 777.

9:00 AM LI.1.2

The icosahedral phase formation and associated structural evolution in the Al-Cu-Fe ternary system have been examined through a novel process. Al-Cu-Fe samples have been produced from the repeated cold rolling and annealing process of the Al, Cu and Fe elemental foils with a target composition of Al42Cu4Fe25.5 (at%). Upon early increments of the rolling and annealing cycles, the elemental Fe foil was dispersed throughout the refined Al and Cu layers. When the rolling and annealing step reached 40 cycles the Al2Cu phase has been observed, but no ternary phases were identified even though additional rolling and annealing cycles were carried out. As it has been reported for mechanical alloying, the stable icosahedral phase could be obtained only after thermal annealing at 650 and 750°C. This is believed that the dissolution of the Al2Cu phase provides a critical step for the formation of the icosahedral phase. The phase evolution in Al-Cu-Fe duplex-casted cold rolling process will be discussed in terms of the identification of the diffusion pathway associated with chemical potential variation during thermal annealing.

9:15 AM LI.1.3
Effect of Boron Substitution on the Formation and Stability of Decagonal Phase in Al-Cr-Fe Alloys. Yasmin Khare1, Conrad Boehr1 and Jean-Marie Dubois1. 1 LS2GM, CNRS/École des Mines, Nancy, France; 2Laboratori Solidi Physici, Institute of Technology Zurich (ETH Zurich), Zurich, Switzerland.

Effect of substitution of minority elements e.g. Si, C, Be, etc. on the formation and stability of quasicrystalline phase has been extensively studied but the effect of Boron substitution on the stabilization of quasicrystalline phase has been sparsely studied. The Al-Cr-Fe system, containing various approximate phases of decagonal phase, has been investigated with regard to the stabilization of quasicrystalline phase. Apart from size factor, some interesting aspects of Boron in metal are the motivation of the present study. One of the important factors is the free energy of intermediate phases influencing the homogeneity range of primary solid solution due to the formation of extended intitial solid solution, which affects the electronic factor responsible for the stability of quasicrystalline phase. Yet another fact which can not be ignored regarding the substitution of boron is the formation of layered structures in many borides up to 55 at. % B. As decagonal structure has been established as a layered structure, thus it can be expected that Boron substitution will enhance the stability of decagonal phase. Along with various approximate phases a slight decagonal phase has been obtained in the system by small addition of Boron. The phases present in the as-cast and sintered Al-Cr-Fe samples have been studied by different thermal methods, x-ray diffraction, transmission electron microscopy, scanning electron microscopy and microprobe analysis. Some salient features of the decagonal phase in terms of growth morphology, surface structure and orientation relationship with approximate structures have been presented. The effect of boron addition has also been outlined.

9:30 AM LI.1.4
Oxygen Effects on Quasicrystal Formation in Zr60Pt20 Melt Spun Ribbons. Daniel Soreide, Xiaoyun Yang, Elena Rozhkova, Matthew Besser and Matthew Kramer, Metal and Ceramic Sciences, Ames Laboratory, Ames, Iowa.

The quenched structure and devitrification behavior of Zr60Pt20 melt spun ribbons containing measured oxygen contents ranging from 184 to 4737 ppm mass were studied. Ribbons containing less than 500 ppm mass oxygen are fully crystallized and consist predominantly of a metal ordered bct-Zr6Pt phase with significant structural quality. Increasing oxygen content to 1058 and 1547 ppm mass produces a transition to an apparently amorphous and to mixed amorphous and quasicrystalline structures, respectively. Samples with further oxygen additions of 2690 and 4737 ppm mass are composed of quasicrystalline and crystalline phases in an amorphous matrix. The results from this study suggest a critical level of oxygen is required to promote glass formation in Zr60Pt20 melt spun ribbons produced at a specified quench rate.

9:45 AM LI.1.5
A Critical Link Between Amorphous Structure and Quasicrystalline Formation in Zr-Based Alloys. Daniel Soreide, Xiaoyun Yang, Z. Liu1, Xiaodong Chen1,1, Dan Soreide2, Matt Kramer, and Cynthia Jenks1. 1Argonne National Laboratory, Argonne, Illinois; 2Department of Science and Mathematics, Cedarville University, Cedarville, Ohio; 1Metal and Ceramic Sciences Program, Ames Laboratory, Ames, Illinois.

In this work, we have used fluctuation electron microscopy (FEM) to provide direct evidence of the role of oxygen on the crystallization of amorphous Zr46Pt30 alloys. It has been speculated widely that the degree of short- or medium-range order in amorphous Zr-based alloys plays an important role on crystallization behavior, with such order necessary to lead to crystallization of quasicrystalline phases. FEM is a direct probe of medium-range order and thus provides unique capability to probe amorphous structures. We have used FEM to probe medium range order in two Zr46Pt30 amorphous alloys that exhibit very different crystallization behavior, with one amorphous Zr46Pt30 alloys prepared by melt spinning forming the metastable...
quasicrystalline phase during devitrification whereas amorphous alloys prepared by mechanical milling do not. TEM reveals significant differences in the arrangement order in these quasicrystalline alloys, suggesting the critical role such order plays in crystallization, and these results and their implications will be discussed. This work was supported by the U.S. Department of Energy, Office of Science and of Energy Efficiency and Renewable Energy, under contract #W-31-109-ENG-38 (ANL) and #W-7405ENG-82 (Ames). Electron microscopy was carried out in the Electron Microscopy

10:30 AM #LL1.6 Unique indexing scheme of decagonal phases based on a six dimensional model. Rajiv Kumar Mandal, A.K. Pramanik, G.V.S. Sastry and S. lele; metallurgical engineering, bharati hindu university, varanasi, up, India. Mandal and Lele [1989] have proposed a six dimensional model for the structural description of the decagonal phases. The integral linear combination of six basis vectors for indexing a physical vector in their model, however, leaves the problem of redundancy in indexing. While revisiting their model we have noted that the condition of a null vector in physical space permits the formulation of unique indexing scheme both in physical reciprocal and direct spaces. We will demonstrate that our scheme, unlike all previously discussed ones, relies only on the information contained in the model. It will also be shown that disfavored spot having equivalent indices possesses identical intensity. This aspect, though equally important, has been totally ignored in the past. We shall substantiate our claim by taking examples from the known decagonal phases. We shall also present parity condition on indices that will be helpful in discussing subtle features of diffraction patterns.

11:00 AM #LL1.7 Composition Rules of Quasicrystals. Chung Dong1,2, Jinping Qiang1, Yingmin Wang1 and Patricia Thiel2,3; 1State Key Lab of Materials Modelling, Department of Materials Engineering, Dalian University of Technology, Dalian, Liaoning, China, 2Ams Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa.

Some simple composition rules of binary and ternary quasicrystals are pointed out and are related to quasicrystal stabilization mechanisms. For a binary quasicrystal of the icosahedral glass type, the composition is mainly determined by topology of medium-scale packing of the atoms in the basic 57-atom icosahedron. A ternary quasicrystal is located at the crossing point of two kinds of specific lines in a ternary phase diagram, which we term e-variant and e0-variant lines, respectively. The e0-variant line, which is a common electronic structure shared by the quasicrystalline and its e0-variant approximants. The e0-variant line, defined by linking the composition of a binary quasicrystal, as approximant, or an fcc-cubic approximant, has the growth pathway of a basic cluster towards final quasicrystalline and crystalline phases along the line. These simple rules are general in quasicrystalline systems. Applications of these rules in two exemplary systems, Al-Mg-Pd and Zn-Al-P, are presented.

11:15 AM #LL1.8 The Stability of Icosahedral Cd-Yb. Georgios Krassas1, Sofia Deloudi1, Andreas Geppert1, Walter Spreitzer1, Amy Ross2 and Thomas Lograsso3; 1Department of Materials, Laboratory of Crystallography, Zurich, Switzerland, 2Ams Laboratory, Ames, Iowa.

What stabilizes quasicrystals? It is still an open quest on whether or not quasicrystals are energy stabilized. In that case, the quasicrystalline state would be restricted to a high-temperature regime. The recently discovered icosahedral phase in the system Cd-Yb could be a possible example of medium-range intermetallic system Cd-Yb shows six binary line phases. One of them is the congruently melting stable icosahedral phase Cd5.7Yb, and another one its cubic 1/3-approximantCd6Yb. Since these phases are line phases chemical disorder can be excluded as essential entropy contribution. The stability of icosahedral Cd5.7Yb was studied as a function of temperature and pressure. X-ray diffraction experiments were carried out on single-crystalline as well as polycrystalline samples in the temperature range 20 K ≤ T ≤ 900 K. High-pressure studies were performed up to 13 GPa. Inter alia, it was found that powders behave different from single crystals. Therefore, also the influence of chemical stress on the icosahedral phase stability was investigated. Time-dependent structural changes at ambient as well as at elevated temperature were recorded after high-energy ball milling of the icosahedral phase at liquid nitrogen temperature. The results indicate a low-temperature instability of this binary quasicrystal.

11:30 AM #LL1.9 First-Principles Study of Order-Disorder Transition of Cd5Ca. Kusaii Nara1 and Yasuki Ishii2; 1SORST, Japan Science and Technology Corporation, Kawasaki, Suita, Japan, 2Department of Physics, Chuo University, Bunkyo-ku, Tokyo, Japan.

Cd5Ca is a cubic 1/3-approximant of the binary icosahedral quasicrystalline Cd5Ca. The structure of Cd5Ca is described by hcc packing of four-layered shells at room temperature. The innermost shell is a Cd5 tetrahedron, where the eight vertices of a cube are occupied with half occupancy. Recently, some anomaly in the temperature dependence of the electrical resistivity and the specific heat at 110 K were found in Cd5Ca, and they seem to be an order-disorder transition originated in the orientational ordering of Cd5 tetrahedra. These anomalous behavior were also observed in Cd6Ca. We perform first-principles structural calculations including 168 atoms in a cubic unit cell. Calculations are performed with a pseudo-potential technique and a plane-wave basis set. We will try to calculate the energy cost owing to different orientations of the tetrahedron at body center of the cubic unit cell. We will discuss an energetically favorable ordering of the central Cd5 tetrahedra and a relaxed structure of atomic shells for each ordering. [1] T. Tamura, Y. Murao, S. Takesuchi, M. Ichihara, M. Isobe and Y. Ueda, Jpn. J. Appl. Phys. 41, L524 (2002); [2] S. K. Bhansali, A. Bucher, P. Manfrinetti and S. M. Pashalwar, J. Phys. Condens. Matter 14, 517 (2002)

11:45 AM #LL1.10 Order-disorder transition in a Cd-Ga quasicrystal approximant. Michael Widom1 and Marek Milonjevic2,3; 1Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania, 2Institute of Physics, Slovakian Academy of Sciences, Bratislava, Slovakia.

The stable Cd-based icosahedral quasicrystals have cubic approximants of Pearson type e184 based on body-center-cubic packings of icosahedral clusters. For Cd-Ga-Cr (and also Cd-Yb) the innermost cluster shell consists of a single tetrahedron which takes one of two possible orientations consistent with the cubic symmetry of the approximant. This tetrahedron orientation defines an incommensurate local state variable. First-principles total energy calculations determine the interaction energies between tetrahedra in adjoining clusters, which turn out to be antiferromagnetic in nature. Monte Carlo simulations of this BCC antiferromagnetic model reveal an order-disorder transition at about T=600K, consistent with experimental observation.

SESSION LL2: Synthesis and Structure II
Chair: Cynthia Jenks
Monday Afternoon, December 1, 2003

1:30 PM #LL2.1 Crystal chemistry and electronic structure of magnesium based Mackay icosahedron type approximants. Guido Kreiner1, Yuri Moguliukov1, Daniel Gruner2, Christina Kudla3, Julien Mankou1 and Melanie Schnepp1; 1Inorganic Chemistry, Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany, 2Toris GmbH, Witten, Germany.

In order to obtain reliable experimental information on the long-range order, the role of the valence electron concentration and the type of chemical disorder for Mackay icosahedron type quasicrystals approximate phases of binary and ternary magnesium alloy systems have been investigated. Mg-Pd, Mg-Ag, Gd-Mg-Ag, Gd-Mg-Pd, Al-Mg-Pd and Gd-Mg-Zn alloys were prepared by melting mixtures of high-purity elements in cleaned tantalum crucibles. Lancing and sealing by arc welding was performed under dry argon atmosphere. The Ta containers were encapsulated in evacuated and sealed quartz ampoules for appropriate heat treatments. For sample characterization we used chemical analysis, X-ray powder and single crystal diffraction, metallography, thermal analysis, SEM, EDS and WDS. Electronic structure calculations were carried out within the LMTO-ASA framework. An overview is presented on the crystal structures, homogeneity ranges and physical properties including the following intermetallic phases: Mg9Pd, Mg5Pd4, Mg5Pd9, Mg7Pd2, Mg9Pd2, Al17Mg94, Ag7Mg26, Ag1Mg, Gd12Mg11Al6, Gd38-xMg52x+xPd21y, Gd55-xY3Mg48-xPd13-4x, and GdMg3Pd2. Most phases are complex intermetallic alloys having a high degree of icosahedral structural order, e.g. Mg9Pd, Mg5Pd4, Al17Mg94, Ag7Mg26, Gd58-xMg52x+xPd21y and Gd55-xY3Mg48-xPd13-4x with the Mackay icosahedron as fundamental structural unit. The phase and cluster stability and the long-range order display a strong dependency on the valence electron concentration and the type of chemical disorder.

2:00 PM #LL2.2 Ab initio structure determination of quasicrystals via single...
The standard approach for structure solution of ordinary crystals begins with solving the phase problem. We can take similar step in the case of quasicrystals nowadays. The low density elimination (LDE) method can solve the phase problem in quasicrystals, and provide electron density maps in high-dimensional space. The LDE method is an ab initio phase determination method based on a simple density modification approach in the real space. Although the reconstructed density might not be complete, because of limitation of the phase reconstruction procedure itself, the reconstructed density gives us information about location of occupation domains (ODs), and size and shape of them. Moreover, we can specify which OD contain heavy element. Local atomic shell structure, so-called cluster, can be directly found from a geometrical investigation of the reconstructed density, and this is less affected by quality of the density. With these knowledge, therefore, one can construct a reasonable ideal atomic model based on the cluster model for structure refinement. The reconstructed density can be verified in process of structure refinement, or more easily by comparing the local atomic shell structure with that of known approximate structures if appropriate approximate crystals exist. We applied the LDE method to solve different types of icshedral quasicrystals, A15-TM (TM=transition metal), Mg-Zn-RE (RE=rare earth) and Ca-Yb.

3:30 PM LL.2.3 Stability of quasicrystals in Al-Co-Cu, B-Th and B-Co-Ti systems, Marek Michalski1,2, and Michael Widoms1,2, Department of Physics, Carnegie Mellon University, Pittsburgh, Pennsylvania, 1Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovak Republic. We identify the Al5-Co5-Cu2 phase (pentagonal symbol P44) as an approximate phase in a novel type of decagonal quasicrystal. Generalization of its structure leads to a family of quasicrystalline approximant structures based on hexagonal-B003-15-120 tiling geometry. Ab-initio total energy calculations indicate metastability of the model decagonal quasicrystal structure in this ternary system. The B4-Co (pentagonal symbol P42) and B2-Co-Ti structures are classified as an approximant phases of the decagonal quasicrystal based on the geometry of the square-triangle tiling. Qualitative stability of a model quasicrystal approximant tilings, based on ab-initio total energy calculations, are reported.

2:45 PM LL.2.4 Simulation of Disorder in Decagonal Al-Co-Ni Quasicrystals, Miroslav Klobou, Thomas Weber and Walter Steurer, Department of Materials, Laboratory for Crystallography, Zuerich, Switzerland. The origin of quasicrystalline stability is a challenging and still unsolved question. There are two fundamental different approaches: energy- or entropy-stabilization. Former would mean that quasicrystals are a ground state of matter, latter that they are purely high-temperature states. A key to answer these questions is the evaluation of short- and long-range order correlations in quasicrystals as a function of temperature, which can be obtained from an analysis of the diffuse intensities. The decagonal quasicrystal with composition AI5Co5Ni15 (AI5-Co5Ni15), the so-called Edagawa phase [1], is a superstructure of the nickel-rich basic decagonal Al-Co-Ni phase [2]. It shows an extraordinary richness of complex scattering, including sharp satellite reflections, as well as one-, two- and three-dimensional diffuse diffraction features. In the present studies, we focus on the diffuse features inside the Bragg layers. Disorder is simulated on different scales, ranging from pentagonal bi-pyramids having a diameter of about 6 Å to clusters with 204 diameter. The structural models of the clusters are based on electron microscopy studies. Furthermore, thermal diffuse scattering (TDS) and phonon diffuse scattering (PDS) are calculated in a five-dimensional description. TDS and PDS have been identified to constitute the major part of the experimental diffuse intensities inside the Bragg layers. The disorder structure is examined by translating TDS and PDS into three-dimensional structural information based on structural unit cell as clusters and changes in orientation and interferences among themselves. [1] Edagawa, K. et al., Suzuki, K. & Tanaka, S. Phil. Mag. Lett. 60: 181-188 (1992). [2] Steurer, W., Hoibach, T., Zhang, B., Kek, B. & Lüdtke, R., Acta Cryst. B. 49: 661-675 (1993). [3] Ake, E., Sinits, K. & Tseck, H. P. et al., Phys. Status Solidi, 1840: 4095-4102 (2000).
corresponding 1/1-cubic approximants rather than the quasicrystals themselves. The electrical resistivity, thermoelectric power, and thermal conductivity of the Al₅₇Re₃₅(Ni₃₆Mn₁₄Re₂) (7 < x < 12) 1/1-cubic approximant. A large thermoelectric power exceeding 1,000 µV/K and a low thermal conductivity less than 1.2 W/mK were observed for these 1/1-cubic approximants. The electrical resistivity in these approximants was kept below 1,000 µohm at room temperature, which is more than one order smaller than that of the corresponding quasicrystals. As a result of the large thermoelectric power, the low thermal conductivity, and the low electrical resistivity, a large figure of merit Z ≃ 0.21 at the room temperature LMTO-ASA band calculation on the reliable atomic structure refined by the neutron scattering. Rietveld analysis was employed to precisely determine the electronic structure of the Al₅₇Re₃₅(Ni₃₆Mn₁₄Re₂) 1/1-cubic approximant. We calculate the thermoelectric power using the electronic density of states thus determined and Boltzmann transport equation under the assumption of the energy independent group velocity and the energy independent mean free path over a small energy range of 10 keV centered at the chemical potential. The calculated values of the thermoelectric power show fairly good agreement with the measured ones not only in the absolute value but also in their temperature dependence. The origin of the low thermal conductivity and low electrical resistivity are also discussed in terms of the atomic structure and the electronic structure. On the basis of the present experimental observations and numerical calculations, we show advantages in employing the 1/1-cubic approximants as a potential thermoelectric material over the corresponding isocubical quasicrystals and even commercial thermoelectric materials.

4:30 P.M. LL4.3 Electrical properties of Cd(Yb, Ca) quasicrystals and their approximants. Ken Minoda, Ryutji Tsumura and Shin Takeuchi. Department of Molecular Science and Technology, Tokyo University of Science, Noda, Chiba, Japan.

The binary Cd(Yb, Ca) quasicrystals and their approximants are considered to be free from chemical disorder. We have studied the electrical properties of these compounds in order to obtain insight into the intrinsic properties of the quasicrystal. As a result, we have found that the approximants Cd6Yb and Cd6Ca exhibit metallic behaviors such as positive temperature coefficient of the resistivity. By contrast, the quasicrystals Cd6Yb and Cd6Ca display a distinctive resistivity maximum at low temperature and negative temperature coefficients at higher temperatures, the latter of which being a common property of the ternary quasicrystals. The difference in the electronic transport between the quasicrystal and approximants means that the coherence length of the conduction electrons in the quasicrystals are longer than 1.5 nm, i.e., the Inertie constant of the 1/1 approximants. The results of the specific heat, magneto-resistivity on the binary compounds will be also demonstrated in comparison.

4:45 P.M. LL4.5 Path to Strong Insulating Transport Properties in Bulk AlPdMn. Ralph Lewis Rosenbaum1, Yung-Liang Zhong2, and Juhn-Jong Lin3. 1School of Physics & Astronomy, Tel Aviv University, Ramat Aviv, Israel; 2Department of Physics, National Tsing Hua University, Hsinchu, Taiwan; 3Institute of Physics, Academia Sinica, Taipei; 4Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan.

Electronic transport measurements have been made on bulk isocubical Al₁₁₁Pd₁₁₁Re₇₂₅ (75 quasicrystals (QCs) samples, having increasingly larger resistance temperature ratios, R = R(300 K)/R(300 K). Data were taken between 0.3 K to 300 K and in magnetic fields up to 17 T. Both the zero field resistivity and the magnetoresistance changed from metallic behavior to weakly insulating behavior to highly insulating behavior, as the resistance temperature ratios of the samples became larger. For the insulating samples, the resistivity r followed an inverse temperature power law as r ∝ T⁻³ where 0.3 < x < 1.2 for increasingly insulating samples. The weakly insulating QC samples showed no saturation in the resistivity down to 0.25 K. In contrast, the highly insulating QC samples exhibited saturation behavior of the resistivity below 4 K. A simple model yielded a good fit to the highly insulating data. We acknowledge Prof. Shui-Tien Lin and Drs. Cheng-Ben Wang and Sh-Wen Wu of the National Cheng Kung University in Tainan, Taiwan, for providing us the QC samples. This work was partially supported by the Taiwan National Science Council to Prof. J.J., Lin and S.T. Lin. A portion of this work was performed at the National High Magnetic Field Laboratory, supported by the NSF Cooperative Agreement No. DMR 9620505 and by the State of Florida.
ial-octahedral quasicrystals and their approximants that have received much attention, such as the first quasicrystal i-AlMn, the first stable icosahedral quasicrystal i-AlSiMn, the L1_0 and i-AlPdMn phases, and the new quasicrystals i-CdYb and i-CdCa.

9:30 A.M. LL4.4
Electronic Structure of Al-Cr-Re Intermetallics, Belin-Ferre Esther1, Danhkhzl Zolot2, Fontaine Marie-Francoise1, Thirion Jean1, de Weert Marie-Cecile3 and Dubois Jean Marie4; 1LCMPMR UMR7614, Paris, France; 2Solid state physics, Eotvos University, Budapest, Hungary; 1LSGM, EMN, Nancy, France.

It has been shown recently that wetting of quasicrystalline and related intermetallics surfaces by water differs from Al-Cu-Fe to Al-Cr-Re compounds and depends on the densities of states at the Fermi level of the bulk specimens. Whereas the electronic structure of Al-Cu-Re systems has been widely investigated, to the best of our knowledge no such data is available for Al-Cu-Re alloys. This has motivated the present experimental study of the electronic structure of various Al-Cr-Re samples and two or approximations of the decagonal quasicrystalline compound. The paper will report the results obtained for the valence band of these systems as probed combining the X-ray emission and X-ray photoemission spectroscopy techniques. Emphasis will be on the hybridizations at the Fermi level and the electronic interactions between the two transition elements. Hospitality by the Institute for Solid State Physics of the Technical University of Vienna (Austria) and assistance by Dr. Herbst Mueller are warmly acknowledged.

9:45 A.M. LL4.5
Photoemission spectroscopy of the Cd-based quasicrystals and approximants, Ryuii Tsurumaru1, Ken Minoda2, Chico Asaki3, Shin Takeuchi4, Tsunehiro Takeuchi5, Takayuki Kita6, Takanobu Yokoyama7 and Shiku Shin8; 1Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan; 2Department of Materials Science, Meiji University, Tokyo, Japan; 3Department of Materials Science, National Institute of Technology, Nagaoka University of Technology, Nagaoka, Niigata, Japan; 4Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba, Japan.

We have performed a series of photoemission (PE) experiments of Cd-based quasicrystals and approximants, such as CdYb, CdCa, CdY, etc., using high-resolution ultraviolet PE spectroscopy. As a result, we have observed a sharp Fermi edge in all the studied compounds, and also a distinctive intensity maximum just below the Fermi energy in the case of the Cd-Ca compounds. Comparison of the PE spectra with the calculated DOS implies that the maximum in the valence band PE spectra is partly due to hybridization between Cd sp and Ca d states. In order to obtain more insight into the origin of the maximum we performed resonant PE spectroscopy of the Cd-Ca quasicrystalline across the Cu 2p-3d threshold, i.e., from 345 to 352 eV binding energy. The results show that the maximum in the on-resonance PE spectra is considerably enhanced as compared with the off-resonance PE spectra, indicating that the occurrence of the sp-d hybridization in the Cd-Ca quasicrystal. The results of the all Cd-based compounds are presented.

SESSION LL5: Properties III - Mechanical Properties I
Chair: H.R. Trebin
Tuesday Morning, December 2, 2003
Fairfax A (Sheraton)

10:30 A.M. #LL5.1
Plasticity of Icosahedral Al-Pd-Mn and Zn-Mg-Dy quasicrystals, Marc Heggen, Michael Feuerbacher and Knut Urban; Institute of Solid State Physics, Research Centre Juelich, Juelich, Germany.

The plasticity of icosahedral Zn-Mg-Dy single-quasicrystals was investigated using uniaxial compression experiments at different strain rates and transmission electron microscopy. The evolution of the dislocation density with strain was determined and planar defects such as matrix boundaries, stacking faults and phason defects were observed and characterized. The presence of matrix phases, in particular, provides a deeper insight into the mechanism of dislocation motion, since they allow for an independent determination of the planes of motion. Plastic deformation was shown to be mainly governed by dislocation glide. A constitutive model describing the plasticity of icosahedral quasicrystals (Feuerbacher et al. 2001) was applied to icosahedral Al-Pd-Mn over a wide range of experimental conditions. The model incorporates the evolution of the microstructural parameters. The first, in crystals, is the dislocation density, the second is a quantization-like order parameter that accounts for deformation-induced disordering and thermally activated reordering of the quasicrystal structure. Significant strain-rate dependence was found which can be understood by the interactive evolution of these two microstructural parameters. Feuerbacher, M., Schull, P., Etrin, Y., and Brechet, Y., (2001) Phil. Mag. Lett., 81, 473.

11:00 A.M. LL5.2

The plastic deformation of quasicrystals (QC) is ruled by two types of singularities of the QC order, singularities of the phonon strain field, and singularities of the phonon strain field. In the framework of the general topology theory of defects, both types of defects appear as distinct components of the same entity, called a dislocation. Each of them can also be given a description in terms of more classical concepts, within a detailed analysis of the Volterra process: (a) the phonon singularity breaks some symmetry of translation, represented by Burgers vector bpg; it is akin to a perfect dislocation (b), the phason singularities (there are many attached to each bpg-dislocation), that we call matching faults, are dipoles of dislocations whose Burgers vectors are of a special type; they do break not only a particular translation symmetry but also the class of local isomorphisms of the QC. In fact, such dipoles, if they open up into loops, bound stacking faults. Thus a phason singularity is an imperfect dislocation. A mismatch is nothing else but an elementary matching fault. Relations between bpg, the shape of the dislocation, and the distribution of matching faults, will be discussed. M. Klemm Phasons and the Plastic Deformation of Quasicrystals, Eur. Phys. J., B11 (2003) 315-325.

11:15 A.M. LL5.3
Low Temperature Deformation Mechanisms of AlPdMn Quasicrystals, Michael Teocic, Anne Prout1, Joel Bonneville1, Jacques Rubier2 and Patrick Cordier2; 1Physics, University Of Poitiers, Classeeau Futuroscope, France; 2Physics, University of Lille, Villeneuve d'Ascq, France.

AlPdMn quasicrystalline specimens are known to be drastically brittle at low and intermediate temperatures, while at high temperature they exhibit a plastic behaviour which has some similarities with superplasticity. In the ductile temperature regime, it has been established that plastic deformation takes place by dislocation motion. The high brittleness-ductility transition temperature (BDTT) clearly suggests that diffusion processes are required to plastic flow, but the microscopic mechanism by which dislocations move in this non-periodic structure is still an open question. An arising question is therefore to know if conservative dislocation movement can be produced in this quasiperiodic structure. In the present work, we have used a multi-axial technique with an uniaxial confined medium in order to investigate the plastic behaviour of AlPdMn specimens at temperatures far below their BDTT. The confining chamber has been designed to apply concentrically large confining pressures and high uniaxial stresses. The drawback is that the uniaxial stress cannot be measured. Such a technique has been applied to plastically deform AlPdMn specimens with a confining pressure of 5 GPa at temperatures ranging from 263K up to 673K, i.e., temperature at which diffusion processes can be reasonably assumed to be negligible. The microstructures have been examined, prior to and after plastic deformation, with a JEOL 100CX microscope operating at 200 kV. Microstructural observations indicate that the deformation microstructure evolves with deformation temperature. At room temperature, strips with high dislocation densities are the dominant feature of the microstructure. A careful examination of the dislocations inside the strips indicates that they moved by a glide process. Few events of dislocation climb are as well observed. Increasing temperature, more and more dislocation climb events are observed. A climb multiplication mechanism is proposed to explain the observed dislocation geometrical configurations.

11:30 A.M. LL5.4
Dislocation mechanisms in AlPdMn quasicrystal, Frederic Mignomi, Michael Feuerbacher, Lionel Bresson, Denis Grisins and Daniel Caille, 1CEMES-CNRS, toulouse, France; 2IFF, juelich, Germany; 3LEM/ONERA, chaloul, France.

Most models of quasicrystalline plasticity rely on dislocation glide mechanisms controlled either by Peierls-type mechanisms or interaction with chafers. Previous investigations in as grown samples have shown evidence of pure climb. Here, we report new experiments carried out at low temperature, on AlPdMn single quasicrystalline grain deformed at high pressure under compression. TEM observations in samples deformed at 600 K reveal high density of dislocations trailing phonon faults. Contrast analyses show extensive dislocation climb associated with two- and parallel planes to the compression axis and trailing respectively.

681
vacancies/interstitials/point defects. These results can be interpreted by a concerted climb mechanism with exchange of matter between the two dislocation systems. In deformed samples at room temperature, the deformation is heterogeneous and accommodated by non-planar defects. Dislocations have been observed at the head and emerging from these defects. TEM analyses show that dislocations at the head have Burgers vectors belonging almost to the plane of the defect with a near-screw character. These results can be interpreted by crack healing associated with a mode III crack at the head while high-stress incompatibility forces them to be released by emission of climbing dislocations. We report also in-situ heating and/or spreading experiments. They show dislocations moving in 2D, 3D, and 5-fold planes with straight segments in dense 2D directions. After cooling, contrast analyses of the two Burgers vectors indicates that the dislocations are of motion of screw. Annihilation and multiplication have also been observed in agreement with plasticity mechanisms mediated by dislocation motion. Phason fault lines have been observed in the wake of moving dislocations as a fast-relaxation process associated. The impossibility of glide has been discussed when a dipole formed by climb does not annihilate in its glide plane. All these results confirm that climb is the unique mode of dislocation motion in AlPdMn at least at high temperature.

11:45 A.M. LL6.5
Plasticity of decagonal quasicrystals. Peter Schall1,2, Michael Peterhans2 and Knut Urban2,3,1 IDEAS, Harvard University, Cambridge, Massachusetts,2 IPF, Forschungszentrum Juelich, Juelich, Germany.

Decagonal quasicrystals belong to the class of two-dimensional quasiperiodic crystals that may be represented in two spatial directions and periodic order along the third. Some physical properties of these materials are known to show anisotropic behavior. We have grown the decagonal phase in the Al3Ni-Cu system in the form of large single quasicrystals. Compression and tension experiments on single quasicrystals in three different orientations: with the compression axis parallel to, at an angle of 45 degrees and perpendicular to the periodic axis. In addition we have performed a detailed characterization of the microstructure of deformed samples by transmission electron microscopy. The deformation experiments reveal a distinct anisotropic deformation behavior. In the microstructural experiments we find that the periodic slip system is clearly favored over the quasiperiodic slip system.

SESSION LL6: Joint Session with MM4: Quasicrystals from Metallic Glasses
Chairs: Ken Kelton and Dan Srodero
Tuesday, December 2, 2003
Republic B (Sheraton)

130 P.M. *LL6.1
icosahedral Transformation from Supercritical Liquid in Metal-Metal Type Bulk Glassy Alloys. Akihisa Inoue, IMR, Tohoku Univ., Sendai, Miyagi, Japan.

Since the first synthesis of metal-metal type bulk glassy alloys without metalloid element in Mg, In-Ni-Cu- and Zr-based alloy systems for several years between 1988 and 1991, we have deposited a number of bulk glassy alloys in metal-metal and metal-metalloid systems. It is well known that these bulk glassy alloys exhibit unique engineering properties such as high strength, large elastic elongation, high corrosion resistance, good soft magnetic properties and Newtonian flow. We have also noticed that the metal-metal type bulk glassy alloys have unique heating-induced phase transformation in which primary crystallization phase consists only of big cube or icosahedral phase. It has also been reported that the precipitation of icosahedral phase occurs in Zr, V, Hf and Co-based alloy systems containing special additional elements such as Ag, Pd, Pt, Au, Ti or Nb leading to nearly zero or positive heats of mixing against the other constituent elements. In addition, the icosahedral phase precipitates homogeneously at very high nucleation rates from their supercooled liquid and their grain size is as small as 5 to 20 nm. The precipitation of the icosahedral phase in the alloys containing the special elements has been interpreted to result from an increase in instability of supercooled liquid accompanied by an ease of nucleation of icosahedral phase through the introduction of weak bonding sites in the supercooled liquid structure consisting mainly of short-range icosahedral atomic configurations. The first step of this paper is to review alloy systems in which the icosahedral phase precipitates during heating from supercooled liquid, kinetic behavior and microstructure for the precipitation of the icosahedral phase, and mechanical properties of icosahedral bulk alloys in the Zr, Hf and Co-based alloys containing the special elements. The second is to investigate the reason for the special elements in the precipitation of the icosahedral phase.

2:00 P.M. *LL6.2

[Non-]Quasicrystalline, amorphous and nanocrystalline multi-component Al and Zr-based alloys are attractive materials for advanced high-strength applications. Further property improvements are achievable by designing multiphase composite materials with optimized height-scale and interfacial areas of the constituent phases. Such alloys can be synthesized by quenching from the melt or by solid state reaction using mechanical alloying/hall milling techniques. Many studies suggest a linkage between the short-range order of the amorphous phase and the formation of quasicrystals or other related complex intermetallic compounds. These suggestions are based on the idea that the liquid prior to vitrification contains icosahedral short-range order or clusters, which are retained in the solid state even after quenching in the glassy state/supercooled liquid. Moreover, there are speculations that solid state synthesis does not provide the opportunity to form the initial short-range order as proposed in liquid-to-solid processing routes. We have investigated single-phase alloys and multiphase composites containing different volume fractions of (quasi-)crystalline or amorphous phases with different length-scales of the constituent phases prepared by quenching from the liquid as well as by solid state reaction. Examples for the phase formation and the development of the microstructure under different processing conditions, the short-range order and for the thermal stability of the metastable alloys will be given, and critically discussed by considering the underlying thermodynamics and kinetics of metastable phase formation. Data for the mechanical behavior will be presented, revealing that in particular the properties of composite materials in quasicrystal-forming systems can be tuned within a wide range of strength and ductility as a function of volume fraction, size and morphology of the different phases.

2:30 P.M. *LL6.3

In the Zr-Cu-Ni-Al system one of the best bulk metallic glass forming alloys was found. But in a narrow concentration range around the composition of the best bulk glass forming ability (e.g. Zr63Cu20Ni15Al7), formation of quasicrystals either by primary or polymorphic reaction is known to proceed during annealing [1]. Exchange of Cu or Ni by other late transition elements was found to stabilize or deteriorate quasicrystalline formation. The reason for such an influence on the formation of quasicrystals is not known as yet. Recent papers mention for example some evidence that the quasicrystals in these alloys are a hybrid of two structural elements, i.e. the tetragonal Zr4Ni (Al4Cu) and the tetragonal Zr2Cu (MnSi)2 structure, as well as the influence of a positive enthalpy of mixing for at least one of the interactions, namely that between TM and M. Whereas replacement of Cu by Ag is known to result in nanocrystallization of the quasicrystalline phase [2], small Ag additions in the range of 0.5 to 1 at.% reduces the number of nucleation sites significantly, thus allowing growth of rather large quasicrystals. This paper presents a detailed study on the influence of Ag additions on the formation of icosahedral quasicrystals. Electron microscopy with DSC as well as crystallization kinetics allows the separation of the influence of Ag on the relevant crystallization parameter, for example the interfacial energy. Reasons for the observed behavior will be discussed in detail. The results may help to understand the ruling factors on the formation of quasicrystals in Zr-based glasses. [1] U.Kester, J.Meinhardt, S.Roos, H.Liebertz, Appl.Phys.Lett. 69 (1996), 179, [2] J.Suidn, M.Matsushita, A.Inoue, Mater.Sci.Forum 360 - 362 (2001), 73.

2:45 P.M. *LL6.4

Although Zr-based glassy alloys that form a metastable quasicrystalline phase upon partial devitrification have attracted much attention in the last years and several investigations have been performed, the knowledge regarding quasicrystal formation is still incomplete. In order to clarify the role of Al, an element often present in quasicrystal-forming Zr-based alloys, on the formation of the quasicrystalline phase, the devitrification of glassy Zr61.5Ti28 Nb10.5 alloy with 0.75, 2.75, 5 and 7.5 at.% pre-melt spinning was investigated. The crystallization
behavior was studied by isochoral and isothermal thermal analysis, x-ray diffraction and electron microscopy. The devitrification of the ribbons is characterized by the formation of metastable and quasicrystalline phase during the first stage of the crystallization process, followed by successive transformation into intermetallic compounds at higher temperatures even for the alloy with \( x = 0 \). Therefore, Al is not essential for quasicrystalline formation in the present alloys. However, it affects the properties of the amorphous as well as of the quasicrystalline phase. In fact, with increasing Al content, the range of stability of the quasicrystalline phase decreases whereas the stability of the amorphous phase increases, due to the increase of the supercooled liquid region. Thus, it is concluded that although the addition of Al improves the properties of the glassy phase, it has no beneficial effect on the formation of quasicrystals.

3:30 PM *LG6.5
Topological and Chemical Short-Range Order in Undercooled and Stable Melts Forming Quasicrystals and Approximants.
Daniel Barron-Bloch1,2, Jean-Jacques Salvetat1, Jean-Marc Petit1, and Robert Bellissent3. 1Institut Laue-Langevin, Grenoble, France; 2Laboratoire de Chimie, ENSCP, Paris, France; 3Centre de Recherches sur la Matériaux et les Procédés, Grenoble, France.

It was suggested already in 1952 by Frank that an isochronal short-range order should be energetically favored in undercooled melts of systems consisting of atoms of spherical geometry.

This hypothesis was recently experimentally confirmed by diffraction experiments on stable and undercooled melts of pure metals. In this work, systematic x-ray investigations on the short-range order of deeply undercooled melts of quasicrystalline and polytetrahedral phases by electron scattering are presented. For Al\(_{53}\)(Co,Fe) alloy, partial structural factors were determined which allow the analysis of both the topological and the chemical short-range order of the function of the temperature. These experiments indicate an isochronal topological short-range order prevailing in the undercooled liquids which is accompanied by a pronounced chemical short-range order such that the first coordination shell around transition metal atoms consists preferentially of Al-atoms. An enhancement of the topological and the chemical short-range order is observed if the temperature is decreased. The influence of this short-range order on the nucleation behavior of quasicrystalline phases in undercooled liquids is discussed.

4:00 PM *LG6.6
Metastable States During Devitrification of Metallic Glasses. Matthew J. Kramer1, Dan J. Soodak1 and Pete L. Lee2. 1Ams Laboratory, Iowa State University, Ames, Iowa; 2Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois.

High-energy/high-temperature X-ray diffraction was used to investigate the time-temperature transformations in the short-range order (SRO) of Zr\(_{52}\)Re\(_{28}\) and Zr\(_{52}\)Re\(_{28}\)Cu\(_{10}\) alloys produced by rapid solidification (RS) and mechanical alloying (MM). The differences in the total scattering function \( S(Q) \) as a function of time at a temperature ~50 K below the crystallization temperature were determined. After rapidly heating, diffraction data were taken at ~5 minute intervals. The differences in the \( S(Q) \) over this time interval shown that both alloys undergo a structural relaxation prior to nucleation and growth. The RS alloys showed to have SRO dominated by a random polyhedral configuration close to isochronal symmetry. The MM samples have SRO to medium-range order (MRO) which is topologically similar to the MoSi\(_2\)-type structure \( 1/4 \text{mm} \) but chemically closer to the Al\(_5\)Cu\(_3\)-type structure \( 1/4 \text{mm} \). Reverse Monte Carlo (RMC) simulations of the experimentally measured atomic pair distributions were performed to identify the partial pair distributions and differences in local chemical ordering. At nucleation, the RS alloy is transformed to the isochronal phase while the MM alloy forms the Al\(_5\)Cu\(_3\)-type structure. The differences in the transformation pathways between the RS and MM alloy can be understood in terms of the differences free energy of the SRO to the possible metastable structures. The work at Ames Laboratory was supported by the U.S. Dept. of Energy through Iowa State University under Contract No. W-7405-ENG-82. The Metallurgy and Engineering Collaborative Access Team (METCAT) at the APS is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, through the Ames Laboratory under Contract No. W-7405-ENG-82. The Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

4:30 PM *LG6.7
Investigation by Transmission Electron Microscopy, EDX and EELS of Quasicrystalline Phase in Zr-45.7Tl8.3Ni10Co7.5Be27.5 and Ti42Zr25Ni8Cu9Be18 Alloys. Efficiently Be in the Quasicrystalline Formation.
Bertrand Van de Moortele\(^{1}\), Jean-Marie Pelletier\(^{1}\), Won Tae Kim\(^{3}\), Thierry Epieix\(^{3}\) and Jean-Louis Soubeyxroux\(^{1}\). 1GEMPPM, INSA de Lyon, Villeurbanne, France; 2IPMC, EPFL, Lausanne, Switzerland; 3Science and Technology University, Changoe, South Korea, 4CRIET, CNRS, Grenoble, France.

Since the observation of a quasicrystalline phase in a rapidly quenched Al-Mn alloy by Schechtman et al., many materials containing quasicrystals were discovered. In particular, quasicrystal could be observed in metallic glasses during devitrification. Such phases are metastable and disappear when temperature or time of ageing increases. It is well known that an increase of the sequence length from Vit1 (22.5% Be) to Vit4 (27.5% Be) alloy leads to the formation of a quasicrystalline phase during ageing. Also stable quasicrystalline phase has been reported to form during crystallization of an amorphous Ti42Zr25Ni8Cu9Be18. In metallic glasses, the formation of quasicrystalline phase often takes place by a polymorphic transformation, i.e. this phase has its orientation, which is a necessary condition to go from the matrix to the quasicrystal. However very few chemical analyses have been performed on such phases. The composition of these phases is similar to that of the amorphous matrix. The aim of this work is to compare the chemical evolution of two metallic glasses during crystallization with an emphasis of the effect on the formation of quasicrystal. EDX and EELS analyses show that the quasicrystalline phase in the Zr-46.7Tl8.3Ni10Co7.5Be27.5 alloy (Vit4) does not contain Be, indicating that a chemical partitioning takes place during the precipitation. Measurements in the Ti42Zr25Ni8Cu9Be18 alloy indicate an important change in the chemical composition of the Be content on the quasicrystal formation is discussed.

4:45 PM *LG6.8
The micromechanics of amorphous-to-quasicrystalline transformation in a Zr-based bulk metallic glass. Lin Liu\(^{1,2}\), K. C. Chen\(^{1}\), G. K. H. Pang\(^{3}\) and K. Z. Babashah\(^{4}\). 1Department of Industrial and System Engineering, Hong Kong University of Science and Technology, Hong Kong; 2Department of Materials Science and Engineering, Huzhou University of Science and Technology, Zhejiang, China; 3Department of Materials Science and Engineering, Hong Kong Polytechnic University, Hong Kong, Hong Kong; 4Department of Applied Physics, The Hong Kong Polytechnic University, Kowloon, Hong Kong.

A Zr-based bulk metallic glass with a diameter of 2 mm was successfully prepared by the arc-melting process. The phase transformation of the glass was investigated by x-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). It was found that the bulk metallic glass obtained two distinct orthorhombic phases. The first one corresponds to the formation of quasicrystals from the amorphous phase, while the second reaction results from the formation of a stable intermetallic compound from the previously formed quasicrystals. In order to understand the micromechanism governing the amorphous-to-quasicrystalline transformation, high resolution TEM coupled with nanoscale EDX was employed to monitor the structural evolution of the glass with the increase of temperature. It was found that the amorphous-to-quasicrystalline transformation does not follow the traditional nucleation/growth mechanism. Instead, it undergoes a series of inter-processes with the formation of a set of metastable phases. The metastable phases are highly disordered and possess a high density of lattice defects, such as dislocations, stacking faults and nano-twinned lattice ordering. The metastable phases gradually modified with the increase of temperature, and finally fell into the lattice array and symmetry of quasicrystalline EDS revealed that the microstructural evolution involved in the whole process of the phase transformation, suggesting that the amorphous-to-quasicrystalline transformation in the present bulk metallic glass is a non-polymeric reaction, and the transformation seems to be governed by the lattice-softening reaction.

SESSION LL7: Poster Session
Chair: Yasosufi Ishii
Barney Day, December 2, 2003

8:00 PM
Exhibition Hall D (Hynes)

LL7.1 Novel Microstructures and Macrostructural Evolution During Cladding and Remelting of Quasicrystalline Forming AlCuFe on Pure Aluminum. Krishnam Buwawat, Rolf Gahn, Karin Klostergaay and Barry L. Mordike. Metallurgy, Indian Institute of Science, Bangalore, Karnataka, India; 2W, Technical University, Clausthal-Zellerfeld, Germany.

In an earlier work [1], we have shown that it is feasible to form quasicrystalline phases in clad and remelted layers prepared on aluminum substrate with a continuous wave CO2 laser of 2.5 kW power. It has been found that the clad and remelted layers contained cracks and pores and the quasicrystalline phase content in the
microstructure was quite small as compared to the crystalline phases. In order to improve the quality of the clad layers as well as the quasicrystalline alloy, we have changed the process variables by using a higher power laser (5 kW). The higher power is necessary because the interaction of aluminium with CO2 laser is weak. This paper deals with the detailed microstructural evolution during the laser processing. Experimental results reveal the microstructural difference between the clad and remelted layers. The clad layers show two-layered microstructure. The first layer evolves through a regrowth from the substrate by cellular manner and then the cellular front breaks into dendritic triggered by heterogeneous nucleation of Al3Fe. The second layer shows predominantly Al3Fe dendrites. On the other hand, the remelting of clad layers leads to microstructural evolution with four distinctly different microstructural layers. The scanning electron microscopy examinations show the different growth morphologies of phases. The presence of ten-pointed star like as well lath shaped morphology of Al3Fe dendrites have been found in the clad and remelted layers. The transmission electron microscopy analysis reveals the phase morphologies and solidification path ways. The growth of isocrystal phase at the interface of long faulted Al3Fe dendrites by conventional peritectic reaction between liquid and primary Al3Fe is common. The independent nucleation of isocystal phase has been found in the remelted layer. This clearly indicates the different levels of undercooling the liquid has undergone before the nucleation of the primary phase. The novel microstructural formation of the tetragonal omega phase with shell like morphology around the isocystal phase and ten-pointed star like growth of isocystal phase from a central isocystal grain has been observed. [1] K. Chintapally, K. Biawa, S. Bykh, G. Paniukumar, A. Wadat, R. Gukin and B.L. Mordike, MRS Proceedings, 2001, Vol. 643, pp.K15.3-1.K15.3.12

LIT.2

Atomic Short-Range Order in Al-Ni-Co Decagonal Quasicrystals. Hiroshi Abe, Materials Science and Engineering, National Defense Academy, Yokosuka, Kanagawa, Japan.

Diffuse scattering from atomic short-range order (SRO) of decagonal quasicrystals was observed in samples quenched above transformation temperature. By quantitative measurements using anomalous X-ray scattering (three wave length method), SRO diffuse scattering was divided into three pair correlation function, that is, Al-Ni-C and Al-Co. Furthermore, the calculated diffuse scattering is in good agreement with the experimental one, where SRO parameters are determined by Monte Carlo model.

LIT.3

Local Chemical Fluctuation-Induced Structural Variations in 1217N20Co8 Quasicrystals. Yasu Yagi1 and Stephen Pennycott 2.

We investigate local chemical fluctuation-induced structural variations in 1217N20Co8 quasicrystals using first principles density functional total-energy calculations. We find that local chemical fluctuation can cause large structural variations on the central rings of the 2m chains. The relationship between the structural variation and phonon-related defects will be discussed.

LIT.4


Bulk, single grains of the isocohedral Cu48Yb52 quasicrystal phase were examined using high resolution transmission electron microscopy (HRTEM). Foils for HRTEM were electron discharge machined from larger grains on the order of 0.75 cm and mechanically thinned to ~200 nm then electro polished. Examination was performed along the two and five-fold axes of the primitive isocohedral structure. Through focal images were obtained and compared to cluster structure proposed by Tani et al. Nature 408 (2000) 2000 and the analysis based on the YC68 solved by A. C. Larson and D. T. Cromer, Acta Crystal. B, 27 (1971). Image reconstruction of the multiple through-focal series for both the two and five-fold axes are consistent with the local cluster structure of concentric polyhedra consisting of Cd tetrahedra. [1/3 occupied isocohedron], Cd octahedron, Yb octahedron, and tetragonal half octahedron. Edge-sharing of the clusters can result in complete tilting of the 3D projections. Simple matching rules are being investigated to construct a 3-D model.

LIT.5

Three-Dimensional Atomic Structure of Isocohedral Zn-Mg-Y Quasicrystal. Seung-Tae Hong1 and John D. Corbett 2.

We show for the first time that the novel three-dimensional atomic structure of a QC, that of Zn36Mg34Y10, can be derived from single crystal X-ray diffraction data without assuming higher dimensionality. The data were collected with a CCD area detector. About 2000 reflections were measured with λ = 0.80 Å. The Cartesian coordinates were used for the reciprocal vectors on a Fourier map. Fractional indices relative to the three orthogonal 3-fold axes in In symmetry. Assumption centrosymmetry of the QC, among a total of 45 shell of independent peaks, five of the stronger independent peaks were selected for the initial Fourier transformation. All of the possible combination of phases, 23 32, were tried to calculate electron density maps for volumes of 10 x 10 x 10Å3, among which one successful examination showed that only one sensible model was produced. The tentative phases for the other reflection sets were then obtained via an inverse Fourier transformation, and in turn, an electron density map was calculated by Fourier transformation, which presented sharper peaks, and so on. The volume of interest was increased, and the routine was iterated directly to convergence. More than 27,805 atoms were eventually located within a sphere of 80 Å radius. The atom types were assigned according to observed electron densities and the overall stoichiometry. The resulting three-dimensional model has a global isocohedral symmetry and consists of many isolated or interpenetrated isocohedral clusters, each of which is surrounded by a dodecahedron. The model also clearly reveals structural motifs as well as the relationships between them in real space. This approach provides a significantly simpler and more direct way to build a three dimensional structural model, consistent with the observed X-ray diffraction, the measured stoichiometry, and density.

LIT.6

Decagonal AlNiCo: Lattice gas Monte-Carlo on an over-approximated atomic surface. Siddharta Nadh, Mike Wadon1 and Marek Mihalkovic 2.

1 Dept. of Physics, Carnegie-Mellon Univ., Pittsburgh, Pennsylvania; 2 Institute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia.

We investigate the structure of the high temperature decagonal quasicrystalline phase of Al12N20Co8 using a lattice gas Monte-Carlo simulation. To avoid biasing the atomic surface structure an over dense site list with a large fraction of free sites was chosen which permitted the simulation to explore a larger region of perpendicular space. The occupancy on the atomic surface was expanded on harmonic functions to aid analysis and especially to account for the phase's drift associated with the oversized region of perpendicular space. In addition correlation functions of the structure were calculated in both perpendicular and parallel space. Special considerations associated with the over-dense site list and the large approximants used are explored. The results obtained are discussed and compared to experimental determinations of the structure of this phase.

LIT.7

Ti-Zr-Ni and Ti-Hf-Ni Quasicrystals and Approximants. Y. T. Huett, J. T. Hertzell and K. F. Kelton, Department of Physics, Washington University, Saint Louis, Missouri.

Zirconium and hafnium are the two most similar elements known, having almost identical size and chemistry. However, rapidly quenched samples of Ti47Zr53Ni10 form quasicrystals, whereas rapidly quenched samples of Ti47Hf53Ni10 form a high order 3/2 rational approximant to the quasicrystal. Further, the fast-cool samples are different; Ti47Zr53Ni10 cast samples form a C14 Laves phase, while Ti47Hf53Ni10 cast samples form a Ti4Ni-type phase. Both alloys store large quantities of hydrogen, up to a hydrogen-to-metal ratio of 1:7. However, while gas phase charging of the Ti47Zr53Ni10 samples always produces an irreversible hydride phase the hafnium 3/2 RA composition shows little to no hydride formation when charged at the lower hydriding temperatures. To investigate these differences the phases in fast-cool and quenched Ti47Zr53Ni10 alloys were systematically studied using x-ray and electron diffraction. New measurements of the equilibrium vapor pressure as a function of hydrogen concentration are also presented. These show a pressure plateau near 10 nm, a suitable range for possible hydrogen storage applications.

LIT.8

Coherent Lattice Sites between Cubic β-Zr(Pt) and an Isocohedral Phase in Rapidly Solidified Zr80Pt20 Alloys. X. Y. Yao, M. J. Kramer, F. A. Hoshokin, M. F. Besser and D. J. Sierak, Metal and Ceramics Science Program, Ames Laboratory, Ames, Iowa.

Coexistence of a bcc hyperoctahedrally β-Zr(Pt) (Im3n) superstructure and a primitive isocohedral phase (p(1) phase) in rapidly
solidified Zr8Pt20 alloys has been studied by transmission electron microscopy (TEM). Results show that the two phases have a well-defined orientation relationship, and the crystalline match and nearly identical stoichiometry. Orientation relationship can be described as two-fold axes of the p phase are nearly parallel to (110p), (110), (112p) and (112p) axes in β-ZrPt; similarly, five- and four-fold axes have comparable orientation to (110p) and (110p) axes, respectively, in β-ZrPt. The common thing in all the observed orientation relationships is the registry between (110β)-Zr phases and icosahedral (21111) five-fold or (210101) two-fold planes. The space group Invm for both β-ZrPt's and the observed orientation relationship precludes β-ZrPt as an approximant to the p phase, even though they appear to have similar primary interplane spacing of 0.255nm. Both β-ZrPt and the p phase are distorted, β-ZrPt maintains a basic β-Zr Bravais lattice but with icosahedral superstructure. Morphologies and growth habit suggest that the p phase forms first, followed by an easy nucleation of the β-ZrPt on the surfaces of the p phase. To the best of our knowledge, this is the first report on the crystalline phase associated with i phase in rapidly solidified Zr8Pt20 alloys.

L7.7.9 Electrical Properties of Ag-In-(Yb, Ca) quasicrystals and their approximants. Daisuke Tetsuka, Ruiji Tamura and Shin Tsuchida; Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan.

The Ag-In-(Yb, Ca) quasicrystals discovered by Guo et al. are obtained by replacing Cd with equal amounts of Ag and In in the binary Cd-In (Cd-Ca) quasicrystals. The ternary alloys are of particular interest from a viewpoint of the influence of the chemical disorder upon the electronic transport. In this work, the electrical properties of Ag-In-(Yb, Ca) quasicrystals and approximants were investigated in order to gain insight into the influence of the replacement of Cd with Ag and In in the electronic transport. As a result, we have observed that the ternary approximant Ag-In-Yb exhibits negative temperature coefficient of the resistivity with a resistivity maximum at a low temperature, which is similar to that seen in the ternary Ag-In-Yb quasicrystal. The result is in striking contrast with the case of the binary Cd-In system where the approximant exhibits a positive temperature coefficient in the whole temperature region. Such a result may imply that the occurrence of the negative temperature coefficient of the resistivity is a consequence of the chemical disorder that might have been induced by the replacement of Cd with In and Ag.

L7.10 Abstract Withdrawn

L7.11 Low Energy Surface Phonons of Decagonal and Icosahedral Quasicrystals Studied by Inelastic He Atom Scattering. Hem Raj Sharma3, Kushwaha J. Prank,1,2 Wolfgang Thein1,2, Philip Ebnet3, Peter Gille4 and Karlheinz Rieder1,2; 1Institut fu¨ r Experimental physik, Freie Universita¨ ten Berlin, Berlin, Germany; 2Institut fu¨ r Physik und Angewandte Chemie, Ludwig-Maximilians-Universita¨ t Mu¨ nchen, Munich, Germany; 3Institut fu¨ r Festk¨orperforschung, Forschungszentrum Ju¨ rch GmbH, Ju¨ rch, Germany.

With the successful preparation of high structural quality surfaces, it has been possible to measure low energy surface phonons (Rayleigh mode) of quasicrystals by He atom time of flight (TOF) technique. The tenfold surface of decagonal Al5Be4Ni4, the fivefold surface of icosahedral Al15B4P2Mg3 are found to possess well-defined Rayleigh modes with isochronous sound velocities of about 3840 m/s and 3470 m/s, respectively. The observed sound velocities are in good agreement with calculations based on the respective bulk data. The experimental phonon dispersions exhibit quasi-Brillouin zones located at strong Bragg peaks. On the tenfold surface, single phonon peaks are observed up to a surface temperature of 550°C without shift in position indicating that the sound velocity does not change appreciably up to this temperature. The phonon peak intensity decreases monotonically with wavevector and becomes non-separable from the broad background intensity for wavevectors larger than 0.03Å-1.

L7.12 A maximum density principle for surfaces of icosahedral and decagonal quasicrystals. Zoran Papadopoulos1,2, P. Plenatman2, G. Kramer1,2, V. Fournier1, J. Jenks2, L. Leclerc2 and R. Megraji1,2; 1Inst. fuer Theoretische Physik, Univ. Tuebingen, Tuebingen, Germany; 2Inst. fuer Theoretische Physik, Univ. Magdeburg, Magdeburg, Germany; 3Center d’Ingenierie de l’Material, Eole des Mines de Nancy, Nancy, France. 4Arne Lab., Iowa State University, Ames, Iowa; 5Surface Sci. Res. Centre, The University of Liverpool, Liverpool, United Kingdom.

The surfaces of crystals correspond roughly to maximally dense planes of atoms in the bulk of the same crystalline form. Comparing theoretical models of quasicrystals with experimental results, we find that this correspondence breaks down and that surfaces parallel to the densest planes in the bulk are not the most stable. The correspondence is restored by replacing the maximally dense surface with the surface that has the maximum density of the two-dimensional structures on the surface. We study Al5Be4Ni4, an Al-based decagonal quasicrystal and decagonal Al-Cu-Co [1], [2]. [1] Z. Papadopoulos, P. Plenatman, G. Kramer, V. Fournier, T. Cai, C. Jenks, P. Thié, J. Legouz and R. Megraji: A maximum density rule for surfaces of quasicrystals, preprint, cond-mat/9902325 [A. Korotkov, Phys. Rev. Lett. 64 (1990) 200]

L7.13 Corrosion properties of quaternary Al-based quasicrystal thin films. Michael S. Danley3, Alexander N. Khramov4 and Simon Baker5; 1Nonmetallic Materials Division, Wright-Patterson AFB, WPAFB, Ohio; 2University of Dayton Research Institute, Dayton, Ohio; 3University of Dayton Research Institute, Dayton, Ohio.

Aluminum-based quasicrystals are insulator alloys composed of 76.8% of aluminum. Recent work has shown that thin film quasicrystal coatings have unique properties such as very high hardness, low thermal conductivity and very high corrosion resistance to corrosion. However, there exists no comprehensive study on corrosion protection afforded by quasicrystal thin films and the mechanism of protection of various metal alloys. The corrosion related properties of Al-Cu-In-Co quasicrystal coatings have been investigated on AA2024 and AA7075 substrates. Quaternary Al-based quasicrystal thin films were investigated on aerospace Al alloys for corrosion protection applications. Results of microstructural and surface chemistry analyses of the quasicrystal films are presented. The thin film deposition parameters are discussed briefly. The corrosion property protection of the films have been studied by potentiodynamic scan and electrochemical impedance spectroscopy. Microscopy studies and electron diffraction of quasicrystal films have shown that quaternary Al-based quasicrystal thin films possess unique corrosion control properties. Corrosion properties were found to be a function of target composition, deposition parameters, and films structural characteristics. High resistance to prolonged electrolyte attack makes these coatings strong candidates for corrosion protection surface treatment of aircraft Al alloys. These films can be utilized as conversion coatings for Al substrates or incorporated into a full coating system containing an organic primer and a topcoat.

L7.14 LEED Studies of the 10-Fold Surface of d-Al-Ni-Co and Xe Adsorption. Nicola Ferrala1,2, Katarina Rosa3, Martin Greve3, C. Jenks, R. Fisher1, M. Lindroos4, Roman McGrath4 and Renée D’Cluz4; 1Physics Dept. and Materials Research Institute, Penn State University, University Park, Pennsylvania; 2Physics Institute, Tampere University of Technology, Tampere, Finland; 3Institut fuer Kristallographie und Mineralogie, University of Muenchen, Muenchen, Germany; 4Aames Laboratory, Iowa State University, Ames, Iowa; 5Physics Dept. and Surface Science Centre, University of Liverpool, Liverpool, United Kingdom.

A dynamical low-energy electron diffraction (LEED) study of the structure of the clean 10-fold surface of Al72Ni11Co17 at 50 K indicates that the surface structure is consistent with a truncation of the bulk structure determined by x-ray diffraction [1]. This model consists of periodically stacked planes, each of which has a structure based on a Penrose tiling having 5-fold symmetry, with each plane rotated by π/5 relative to the plane below it. In an AlABAl stacking sequence, the LEED intensity data were measured over the energy range 20-450 eV. The calculational approach was similar to that used previously for icosahedral quasicrystal surfaces [2]. Aside from a small amount of surface relaxation in the top surface layer and some intrag głumpling, the best-fit structure is very similar to a bulk truncation. Xe adsorbed onto this surface produces a LEED pattern having 5-fold symmetry, indicative of close-packed Xe islands nucleating and growing in alignment with the quasicrystal crystallographic layers. The observed LEED intensities and the calculated LEED intensities are in agreement, indicating that the growth is layer-by-layer for at least two layers, and that the hexagonal ordering first occurs upon adsorption of the second layer. The incoherent component of the photolysis was measured to be 417 meV. [1] W. Steurer, T. Habich, B. Zhang, S. Kek, R. Lucz. Acta. Cryst. B 46 (1993) 601. [2] M. Gréer, M. A. Van Hove, A. J. Goldman, Z. Shen, S. L. Chang, P. J. Pinheiro, C. J. Jenks, J. W. Andreagg, C. M. Zhong and A. Thesis. Phys. Rev. B 57 (1998) 7828. [3] T. Cai, F. Shi, Z. Shen, M. Gierer, A. J. Goldman.

17.5
Surface Transformations of Quasicrystalline Al-Pd-Mn.
Cynthia J. Jenks, Amy R Ross, Thomas A Lograsso, Josh A Whisley and Robert Barcus, Ames Laboratory, Iowa State University, Ames, Iowa, Sandia National Laboratories, Livermore, California.

 Preferential sputtering, as is well known, causes changes in the surface composition of multi-component materials. To reduce this effect while sputter cleaning surfaces of the quasicrystalline phase of Al-Pd-Mn, He ion bombardment in the energy range 0.5 to 3 keV is often used. The low mass of He helps to equalize momentum transfer to the alloy components. Even so, the topmost surface composition can be changed by a small exposure to energetic He ions, which tends to preferentially remove Al from the surface. We have explored, using low energy electron microscopy, how the structure of the Al-Pd-Mn surface is altered by various He ion sputtering and annealing treatments. The structure appears to be sensitive to small changes in composition and undergoes a number of interesting transformations upon subsequent annealing. In some cases a surface exhibiting 5-fold symmetry is restored while for others a surface with decagonal symmetry is produced. Evidence for a gradual transformation from crystalline to a seemingly quasicrystalline structure is presented.

SESSION LL8: Surfaces and Coatings
Chair: Roman McGrath and Patricia Thiel
Wednesday Morning, December 3, 2003
Fairfax A (Sheraton)

8:30 AM *LL8.1
Self-assembly of Low Dimensional Aperiodic Structures on Quasicrystalline Surfaces. Roman McGrath, Surface Science Research Centre and Department of Physics, The University of Liverpool, Liverpool, United Kingdom.

We have investigated the clean 5-fold surface of icosahedral i-AlPdMn using scanning tunnelling microscopy (STM). The surface has several topologies as a function of annealing temperature, and prolonged annealing at 750 K produces a surface which is macroscopically flat. Atomic resolution images of this surface of i-AlPdMn show the surface to be bulk-terminated, and we show that a Penrose tiling may be constructed on the surface which is consistent with experimental data. The icosahedral i-AlPdMn structure has been also been imaged with high resolution. This surface also has several topologies depending on anneal temperature, and at 1125 K a flat surface is formed. We have shown using LEED and STM data that the surface is consistent with bulk models. The development of the ability to prepare high quality quasicrystal surfaces opens up the possibility of using these surfaces for the creation of overlay systems with unusual symmetries. If such systems can be created, they are potentially of great use as single element quasicrystals, which greatly simplifies the characterization of their properties [1]. With this goal in mind, we have carried out an investigation into the formation of a Cu overlayer on the icosahedral surface of i-AlPdMn. Investigation of the i-AlPdMn system using STM and LEED reveal 2 different morphological growths. Up to 8 monolayers, a layer-by-layer growth appears. From 8 ML up to 20ML 3D island growth is observed (Strunk-Kratzmann growth mode). Although layer-by-layer growth has been monitored closely by STM, atomic resolution is only obtained from the 4th to the 6th layer. A new quasicrystalline LEED pattern is also observed at this coverage. Within these layers, 5 sets of lines following the substrate directions have been observed. Within these lines, 2 spacings have been measured, with a ratio close to the Golden Number. In addition the appearance of these lines follows the Fibonacci sequence. Although some atomic structure is still visible within the AlPdMn host, the system degrades beyond this point to finally vanish around 25ML [1] R McGrath, J. Ledieu, E. Cox, R Diehl, J. Phys Cond. Mater. 14 (2002) R1-R26.

9:00 AM *LL8.2
Quasicrystal as a Promising Supporter and Precursor. Ai-Peng Tai and Smasha Kumerick, National Institute for Materials Science, Tsukuba City, Japan.

Quasicrystals, a new form of ordered matter with forbidden symmetries and quasiperiodicity have been found in several alloy systems. Due to the quasiperiodicity, a quasicrystal is generally brittle and therefore not expected to be used as a structural material. Quasicrystalline powders of the thermodynamically stable Al-base alloys contain elements possessing catalytic activity, obtained readily by casting and crushing, are available commercially. We have developed a potential application of quasicrystal as a support (or precursor) on which metallic and oxide nano-particles responsible for catalytic reactions are promoted by solution leaching. We performed steam-reforming of methanol [CH3OH] to H2 and CO. In a number of Al-base quasicrystalline catalysts. The stable Al-Cu quasicrystals reveal high activity for steam-reforming of methanol, quoted in terms of production rate of H2 for the reaction, reaches 300 1000 mol/mol·h. Being supercritical to the industrial catalysts, the high activity is ascribed to the formation of nanoparticles of Cu and Fe, and network structure of Al oxides on the surfaces due to preferential dissociation of Al upon leaching of the Al-CuFe quasicrystal. The Fe particles are supposed to act as a barrier suppressing grain growth due to diffusion of Cu atoms. This is an indication that the quasicrystal has potential to be developed as a high temperature catalyst. The thermal stability of the quasicrystalline catalyst strongly rely on the leaching condition.

9:30 AM LL8.3
Structure, Property and Metal Thin Film Growth on the Surface of the (Al0.3Pd0.7)5Mn5, an Approximate Crystal. V. Fourniee, J. A. Barcus, M. Shimoda, H.-R. Sharma, A. R. Rossa, T. A. Lograsso, A-P. Tess and P. A. Thiel, LSLG2M, CNRS UMR 7584, Nancy, France. *Department of Chemistry, Department of Materials Science and Engineering, Ames Laboratory, Iowa State University, Ames, Iowa, *National Institute for Material Science, Tsukuba, Japan.

Despite close similarity between quasicrystals and approximant phases, most surface science studies performed so far dealt with true quasiperiodic surfaces and not with approximants. Here we will describe the surface structure of the (Al0.3Pd0.7)5Mn5, an approximant crystal, for which large single grains can now be produced. Because the surface perpendicular to the pseudo ten-fold axis is investigated by low-energy electron diffraction (LEED), x-ray photoemission diffraction (XPD) and scanning tunnelling microscopy (STM), both the coverage and short-range order with pseudo ten-fold symmetry is evidenced by LEED and XPD. STM images reveal a terrace and step surface morphology, with details consistent with a bulk termination of the surface. The bulk structure of the quasicrystal can be described by a sequence of layers stacked along the pseudo ten-fold axis. It appears that the surfaces are formed at monolayer.

Furthermore, for Al atoms strongly bounded at specific lattice sites. The rings must be formed during the surface reconstruction upon annealing and are pretty stable. They are identified as part of the pseudo-Mackay clusters of which the 3D structure can be constructed. Then we study the growth of a Pd thin film deposited by electron beam evaporation. Pd do not form a smooth film but rather 3D particles covering the $\eta$ surface. Pd clusters coalesce with time and are relatively stable upon annealing up to 870 K. Clusters have homogeneous size and their average size increases slightly with film thickness, up to 3 nm in diameter at a coverage of 8 monolayers. The local electronic structure of the clusters is studied by scanning tunnelling spectroscopy and appears to be cluster-size dependent. The transition from metallic to metal-insulator clusters seen at UHV temperature in the UHV environment could be used as a model system to get a better understanding of the origin of this property. High catalytic activity may indeed be related to the peculiar electronic structure of the Pd nano-clusters.

9:45 AM LL8.4
Nucleation and Growth of Metallic Films on Quasicrystalline Al$_2$Pd$_{9.5}$Mn$_{8.5}$ Surfaces. Fako Hayer, J. A. Barcus, P. A. Thiel, Ames Laboratory, Ames, Iowa.

An atomicistic understanding of the nucleation and growth of materials atop quasicrystalline surfaces is important for two reasons. First, it could provide a window on how the step edges of larger OCPs can be correlated to the unique structure. Second, this understanding may be a useful tool for growing "artificial quasicrystals" in the form of pseudomorphic thin films atop quasicrystalline substrates. For the deposition of Al on the 5-fold surface of icosahedral Al$_2$Pd$_{9.5}$Mn$_{8.5}$ different growth behaviors can be observed. Al atoms show smooth growth at low coverages (≤ 1 ML), and rough growth at higher coverages. Also surface alloying can be observed, in which the step edges change drastically and terrace widths increase in a very narrow coverage regime around one monolayer. Also the time dependent behavior of the step edge structures for different coverage regimes up to a few monolayers was investigated to get information on the kinetics and dynamic processes on the terrace and of icosahedral Al$_2$Pd$_{9.5}$Mn$_{8.5}$ independent of different Al coverages and deposition fluxes. We will compare these results to the nucleation and growth behavior of Ag on the 5-fold surface of icosahedral Al$_2$Pd$_{9.5}$Mn$_{8}$ [1], and studies of Al deposition on an icosahedral Al$_2$Pd$_{9.5}$Mn$_{8.5}$ quasicrystal [2]. V. Fourniee, T. C. Cui, A. R. Ross, T. A. Lograsso, J. W. Evans, and P.

866
resulting shifts to lower energies are accounted for mainly by a lattice expansion perpendicular to the surface, suggesting a thermal expansion coefficient of the atomic layers in 24.5 \times 10^{-6}/K, for both surfaces. Subsequently, from several measurements, a Debeye temperature of 288 \pm 7 K is found at 43 eV beam energy for the pentagonal surface and 300 \pm 10 K at 61 eV for the threefold-symmetry surface, respectively. The pentagonal surface is known to be the most stable bulk termination, followed by the twofold and threefold symmetry surfaces. Thus, we evidenced by the microfocus formation of all three symmetry directions on the threefold surface. Even though the different morphologies, the Debeye temperature and hence the corresponding vibrational amplitude of surface atoms shows no significant difference. This means that the atomic bonding forces characteristic of the local neighborhood of an atom are comparable for both surfaces. The similarity of our surface Debeye temperatures to that of the bulk value, suggest that the vibrational modes of the bulk and the surface are also similar, supporting the structural bulk model that incorporates structural voids and thermal vacancies, as reported by various groups.

11:45 AM LIES.8

Aging in Ambient Conditions of the Surface of an Approximate Phase in Al-Fe-Cr System: Modifications of the Chemical Structure of the Surface and Consequences on the Surface Properties, Delphine Veyrs1, Patrick Weisbecker2, Christoph Rupin1, Vincent Fournier1 and Jean-Marie Dubois1;

1L'SG2M, École des Mines, Nancy, France; 2L'SCSM, Université Henri Poincaré, Nancy, France.

In most of the technological applications that have been suggested or which are already on their way to be applied, the Al-Fe-Cr alloys will be used in the form of coatings or thin films. This allows to circumvent their inherent brittleness and to make use of their interesting surface properties such as low surface energy, low friction coefficient and high resistance to oxidation and corrosion. In the case of Al-based quasicrystals or approximate compounds, surface properties must be influenced by the presence of a native oxide overlayer covering the surface. We present experimental results providing evidence that this "passive" layer actually evolves with time upon interaction with ambient air and that this ageing of the surface has a strong influence on its physical properties. The same sample was used for all experiments. It is an Al-Fe-Cr approximate crystal. First, elemental quantification and chemical state of the various elements present at the surface is monitored by core-level photoemission spectroscopy as a function of time of exposure to air of the sample surface. Second, X-ray reactivity measurements are performed for a freshly polished surface and after ageing. The results are in favor of a multilayer structure of the extreme surface: the electronic density, the thickness of each layer and the roughness of each interface can be deduced from fitting the variation of the reflected beam intensity with incidence angle. By combining XPS and X-ray reflectivity, it is suggested that the surface can be modeled as the stacking of three different layers growing onto the substrate. The first layer consists of a thin oxide (mixed aluminum or chromium oxides) on top of the bulk matrix, on which a hydroxide layer develops slowly with time. The third layer is a contamination layer with a high carbon content in contact with the atmosphere. The thickness of the various layers evolves slowly with exposure to ambient atmosphere. This evolution of the surface chemistry influences some of its physical properties. For example, the contact angle of water droplets increases with time, i.e. the reversible adhesion energy of water on the surface decreases upon ageing. The electrochemical behavior is also influenced by measuring the corrosion potential. After ageing, the surface layer behaves like a pure capacitance, i.e. electrical charges can easily accumulate at the interfaces after a sufficiently long exposure to ambient air. This is something that is not observed for a freshly polished surface. Both observations could be related to a modification of the electrical properties of the overlayer, in relation to the chemical variations mentioned above.
mechanism by which SiH loses their energy. We would discuss the results of our investigations on the structural modifications and for any related changes in electronic structure of quasicrystals that might arise from such electronic excitations in the system. For our studies we have chosen a very stable and well studied icosahedral Al-Co-Fe quasicrystallite system generally in form of rapidly quenched ribbons. The experiments were performed in the same regime. In this regime, we systematically deposit various ranges of energy (~ 1.3 keV/Å to 4 keV/Å) in to the system, causing electronic excitations in them. The choice of ions generally was dependent on calculations based on Monte-Carlo simulation and some existing literature work on metals/metallic alloys. The samples were irradiated at fluxes of a few 10^16 to a few 10^17 ions/cm^2 in order to ensure homogeneous irradiation. The effect of these electronic excitations on the electronic structure of the quasicrystals is analyzed by doing in-situ resistivity versus fluence and resistivity Vs temperature measurements. Ex-situ resistivity versus temperature and X-ray diffraction (XRD)/High resolution X-ray diffraction analysis were also made on the same pieces in order to understand the effect of SiH irradiation on quasicrystals. [1] Ratnamala Chatterjee, D. Kanjilal and R. A. Dunlap, Nucl. Instr. and Meth. B, 156, 201 [1999]; [2] R. Chatterjee, A. Kanjilal, U. Tiwari, J. M. Ramillon & A. Dunlap, Sol. State Commun. 120, 284-289, 2001 [3] A. Kanjilal, R. N. Dutta and R. Chatterjee, Vaccum 68, 349-355, 2002. [4] Ratnamala Chatterjee & Alke Kanjilal, ICQ 8 Proceedings, submitted to special issue of J. Non-Cryst. Solids, 1999. [5] D. Dunlap, D. Dunlap, Ratnamala Chatterjee, Y. Cuby, M. Quercquan, E. Elkins, M. Galliou and S. Rouziere accepted for publication in NIM B

2:30 PM LL1.4

As Cast Ti-Zr-Ni Quasicrystalline Alloys with Excellent Mechanical Properties. Jianhui Qiang, yijingyang Wang, Zhiwei Yu,2 Cuimin Bo2 and Chiung Ting Dong1, 2 Institute engineering, Dalin university of technology, Dalin, Liaoning Province, China; 1The Institution of Metal and Technology, Dalin MaritimeUniversity, Dalin, Liaoning Province, China; 2State Key Laboratory for Materials Modification by Laser, Iion and electron Beams, Dalin University of Technology, Dalin, Liaoning Province, China.

Bulk Ti-Zr-Ni quasicrystalline alloys were directly prepared by sputter-casting in a water-cooled copper mould. The as-cast samples contain mainly an icosahedral quasicrystal (I) coexisting with minor α-Ti/Zr and/or CuI lines phase. According to compression and indentation tests at room temperature the 1 phase-based alloys α-Ti/Zr+ have a hardness of 5.5GPa and a fracture strength over 1000MPa which is extremely high in comparison with Al-based quasicrystalline alloys. The Young’s modulus is in the range of 23-26GPa. In particular, the as-cast Ti60Zr25Ni15 alloy exhibits an elastic deformation capability of 4% under uniaxial compression, which is about 4 times as large as that of the Al-based quasicrystals and is even comparable with many ZEBON bulk metallic glasses. The quasicrystal fracture morphology points to a brittle fracture mechanism.

2:45 PM LL1.5

Mechanical Spectroscopy of the Formation of Quasicrystalline Order in Rapidly Quenched Ti- and Zr-Based Alloys. Hans-Rainer Sinning, Igor S. Golovin and Adrian Jams, 1 Institute for Materials, Technical University of Braunschweig, Braunschweig, Germany; 2National Institute for Materials Physics, Bucharest, Romania.

In several rapidly quenched Ti-Zr-Ni-Al and Zr-Ti-Co-Ni-Al alloys forming icosahedral quasicrystals, the gradual development of quasicrystalline order was studied by means of mechanical spectroscopy (vibrating-reed technique), which includes the annealing behavior of both Young’s modulus and mechanical loss spectra. In particular – since these alloys are known for their good hydrogen absorption properties – the Snook-type relaxation peak of hydrogen was used as a probe to monitor changes in the polycrystalline short-range order of the metal matrix. Depending on the initial structural state after rapid quenching (amorphous, nano-quasicrystalline or poly-quasicrystalline), different types of transformation and ordering behavior may be distinguished. Among these, the initially nano-quasicrystalline (α×X-ray amorphous) state is characterized by the strongest relative changes of Young’s modulus during annealing (examples: T45Zr45Ni15, T15Zr25Ni40Ag5). Surprisingly, an order-induced narrowing of the hydrogen relaxation peak is then found only in the inter annealing stages where the irreversible increase in Young’s modulus is already completely: apparently, these two properties are sensitive to completely different types of ordering processes. The narrowing of the hydrogen peak is more pronounced for particularly larger grain, well-developed polycrystalline samples [e.g., Ti4Zr2Ni20 or T15Zr25Ni20] and the only text type of the quasicrystalline order is reached within the grains. Quasicrystals of different compositions are characterized by considerable differences in position and width of the hydrogen relaxation peak, whereas these quantities are almost indistinguishable between amorphous and quasicrystalline phases of the same composition. These results may add some new aspects to our understanding and classification of cluster structures in both metallic glasses and icosahedral quasicrystals. Financial support by the DFG Priority Programme 5 Quasicrystals (grant Nr. SI 408/81) is gratefully acknowledged.
The unusual behaviors reported for the electronic transport properties of quasicrystalline (QCs) strongly suggest that quasicrystalline alloys should be used at the baseband with semiconductors. Thus, QC's bridge the gap between semiconducting materials and metallic ones, a very promising position in the quest for novel thermoelectric materials (TEMs). Furthermore, the thermal conductivity of M Os is unusually low for a metallic alloy. This property is particularly remarkable in the light of Stach's phonon-glass/electron-crystal proposal for promoting TEMs. In this talk, we address the question regarding whether the purported anomalies in the transport properties of QCs may render them as promising materials for thermoelectric applications. Such a possibility has been recently discussed by considering a number of experimental results. We have to be close to our QC models to draw new thermoelectric and other technological applications such as bearings, leading gear and engine parts, where thermal and mechanical conditions are prime importance.

4:30 PM LL10.4
Synthesis of Quasicrystalline Phases by Mechanical Alloying of Tia4Zr3Sn3Ni 7 (0 ≤ x ≤ 16) Powder Mixtures, and Their Hydrogen Storage Properties. Akito Tokinami1, Nakvi Inu2 and Kenneth F. Kelton3, 1Department of Mechanical Engineering, Shibuara Institute of Technology, Saitama, Saitama, Japan; 2Graduate School, Shibuara Institute of Technology, Saitama, Saitama, Japan; 3Department of Physics, Washington University, St. Louis, Missouri.

We have previously reported that a Tia4Zr3Sn3Ni 7icosahedral (i) quasicrystal phase produced by mechanical alloying (MA) could store about 9% hydrogen (H/MA ≈ 1.6) indicating its potential as hydrogen-storage materials. In this study, MA of Tia4Zr3Sn3Ni 7 (0 ≤ x ≤ 16) elemental powders was performed to investigate the possibility of the i-phase formation. Their hydrogen storage properties were measured and compared with those of the Tia4Zr3Sn3Ni 7 + i-phase, and the effect of substitution of zirconium with titanium was discussed. As same as the Tia4Zr3Sn3Ni 7+powder mixtures, MA formed amorphous phases directly, and subsequent annealing at 853 K preserved the i-phase and its type crystal phase for all powders in this study. The α-titanium was also produced in titanium-rich powders after annealing. The quantitative constant of the i-phase and the lattice parameter of the Ti3Ni type crystal (fcc) decreased linearly as the hydrogen concentration in the powder increased. The maximum hydrogen concentration that could be loaded in the annealed powders after electrochemical hydrogen charging was about 63 at. % (H/MA ≈ 1.7). No chemical compositional dependence on the maximum hydrogen storage was observed. Hydrogen desorption temperatures, measured by thermal desorption spectroscopy equipped with a quadrupole mass analyzer, increased with increasing titanium concentration in the powder.

4:45 PM LL10.5
The Evolution of Short-Range Order in Ti-Hf-Ni Alloys with Hydrogenation: Annealed and Quenched. Ana Salvador1, Van P. Haughton2, 1CICE, University of Cergy-Pontoise, Cergy-Pontoise, Cergy, France; 2ULRHE, Centre Universitaire Paris-Sud, Orsay, France.

Ti-based quasicrystals and related crystals have a large capacity for hydrogen storage [1], presumably due to the large number of tetrahedral sites in their structure, which are favorably occupied by hydrogen. Ti-Zr-Ni and Ti-HfNi quasicrystals can absorb up to two hydrogen atoms for each metallic atom, making them candidates for hydrogen storage materials. The short-range order in 3/2 crystal approximant and amorphous TiH2Ni alloys was determined by EXAFS experiments, and compared to that obtained previously in Ti-Zr-Ni alloys [2, 3]. The alloys were loaded to different hydrogen-to-metal ratios (H/M) between 0 and 1.7 in order to follow the evolution of the local structure with hydrogenation. In Ti-Zr-Ni and non-hydrogenated alloys, the local atomic structure in the Ti-HfNi 3/2 crystal approximant is similar to that in the Ti-Zr-Ni alloys, icosahedral quasicrystal or 1/1 approximant, even around the Zr and H atoms. However, it is somewhat different in amorphous TiH2Ni alloys. After hydrogenation, drastic changes are observed in the local structure, with modifications of the atomic distances and an increase of the disorder. In the Ti-Zr-Ni alloys, a general increase in all of the nearest-neighbor distances is found, especially for the Zr-Ni (or Ni-Zr) ones, which leads to a remarkable inversion of the atomic sub-shells of titanium and nickel in the first environment of zirconium atoms near H/M = 1. Preliminary results of the EXAFS analysis show similar tendencies in the H/M = 1 region and from H/M = 1 to H/M = 2.5, and from H/M = 2.5 to 3.