

Poster Session 4  
Physical properties

Tuesday, June 15, 2010



## Structural Vacancies in 1/1-AlReSi Approximant Crystals Probed by Positron Annihilation Methods

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The temperature coefficient of the resistivity (TCR) of 1/1-AlReSi approximant crystals changes from positive to negative by a small difference in sample's composition, that is, the nominal Re concentrations [1]. Tamura *et al.* suggested that the localization effect occurs when the icosahedral clusters are fully occupied by Re atoms. By changing the Re concentration, the deviations of occupancy of the transition metal sites are expected to be observed by Rietveld analysis, and some distortions or vacancies will be produced. Indeed, Takeuchi *et al.* have reported the result of structural analysis and the number of vacancies at glue site increases by changing Al and Si concentrations [2]. However, the systematic structural analysis by changing Re concentration have not been reported so far. In this study, we performed the positron lifetime measurement by slow positron beam to probe the vacancy concentration in 1/1-AlReSi approximant crystals with different Re concentrations.

Mother ingots of 1/1-Al<sub>72.5</sub>Re<sub>17.4</sub>Si<sub>10.1</sub>, 1/1-Al<sub>73</sub>Re<sub>17</sub>Si<sub>10</sub> and 1/1-Al<sub>73</sub>Re<sub>15</sub>Si<sub>12</sub> were prepared under an argon atmosphere with an arc-melting furnace, and then annealed at 1093K for 1 hour, 1023K for 24 hours and 1073K 48 hours in vacuum in a sealed quartz tube, respectively. The characterization of the samples was performed by powder X-ray diffraction with Cu  $K\alpha$  radiation. The electrical resistivity was measured in the range between 20 and 300K, and positron annihilation lifetime measurement was performed at room temperature.

We found that the long-lifetime component  $I_3$  increases with decreasing Re concentration. The increase of  $I_3$  means that the vacancy concentration in the sample decreases, because more positrons are back to the surface and more ortho-positroniums are formed at the surface.

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## Possibility of Evaluation of Bonding Nature of Al-based Icosahedral Quasicrystals using Positron Annihilation Rate

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Icosahedral quasicrystals (*i*-QCs) composed of aluminum and transition metals exhibit an unusually high electrical resistivity with a negative temperature coefficient. The bonding nature of these *i*-QCs is considered to be closely related to the peculiar electronic properties and is evaluated by the valence electron distribution.

As for the evaluation of the bonding nature of related materials such as Al-based approximant crystals (ACs), Kirihara *et al.* have obtained the electron density distribution of 1/0-Al<sub>12</sub>Re and 1/1-Al(Mn or Re)Si ACs by the maximum entropy method (MEM)/Rietveld analysis [1], and discussed their bonding nature in icosahedral clusters that correlates with whether the center atoms (or structural vacancies) in icosahedral clusters exist or not. The electronic properties of these materials correlate well with their bonding nature in intra- and inter-clusters. From an analogy of ACs, it is important to confirm the existence of structural vacancies and evaluate the bonding nature of icosahedral clusters to understand the electronic properties of *i*-QCs, which is essential for designing applications, e.g., promising thermoelectric materials [2,3]. In the case of *i*-QCs, while the structural analysis of *i*-Al-Pd-Mn quasicrystals has been reported by Yamamoto *et al.* [4], the electron density distribution of *i*-QCs is difficult to obtain because of the lack of atomic periodicity. Because of this circumstance, establishing a method of evaluating the bonding nature of *i*-QCs for material design remains a challenge.

In this presentation, we will report a promising method of evaluation of bonding nature of *i*-QCs by using positron annihilation rate. Recently, we found a strong correlation between the bulk electrical conductivity and local electron density estimated from the positron annihilation rate around the structural vacancies in icosahedral clusters [5]. The present correlation can be used to discuss the valence electron density and bonding nature in *i*-QCs.

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## INTERMEDIATE VALENCE STATE IN Cd-Mg-Yb QUASICRYSTAL

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Recently, we found that in binary icosahedral (*i*-) Cd-Yb quasicrystal an intermediate valence state is realized under pressure [1]. This means that, through the valence change, the charge degree of freedom on the quasiperiodic lattice is controlled by pressure. Searching for another quasiperiodic system where the valence varies more widely, we measured the Yb valence in ternary *i*-Cd-Mg-Yb quasicrystal [2] under high pressure, using Yb- $L_{III}$  edge X-ray absorption spectroscopy.

Figure 1 shows the pressure dependences of the Yb valence in *i*-Cd-Mg-Yb and *i*-Cd-Yb. The valence in *i*-Cd-Mg-Yb increases more rapidly than that in *i*-Cd-Yb. This indicates that the substitution of Mg with the larger compressibility for Cd leads to a more sensitive pressure effect on the valence, although Cd and Mg are divalent and have similar atomic sizes. Furthermore, the valence tends to saturate above 50 GPa. It is considered that, owing to not only the increased bulk modulus by pressure but also the expansion of the  $4f$  bandwidth, the valence change becomes insensitive to pressure. In this presentation, we discuss how the valence change for pressure has a relationship with the electronic state.

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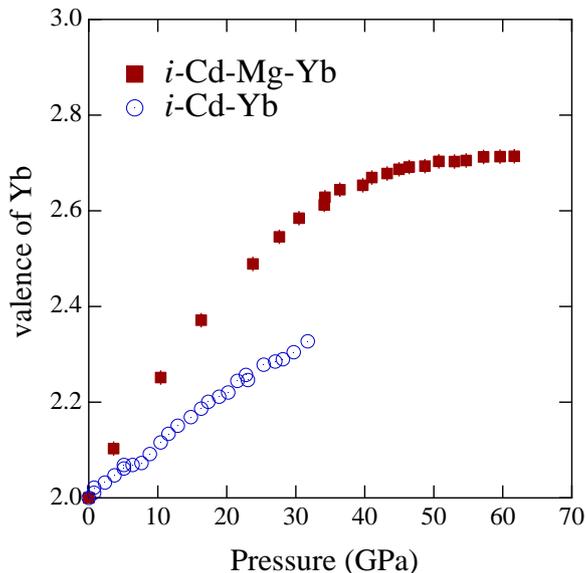


Figure 1: Pressure dependences of the Yb valence in *i*-Cd-Mg-Yb and *i*-Cd-Yb.

## INTERNAL FRICTION STUDY OF ICOSAHEDRAL QUASICRYSTALS AND THEIR CRYSTAL APPROXIMANTS

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The internal friction was measured for Al-Pd-Mn and Al-Cu-Fe icosahedral(i-) phases and their corresponding cubic approximant phases in a forced flexural-oscillation mode in a frequency range of 0.05 – 10 Hz and a temperature range of 300 – 873 K. For the Al-Pd-Mn i-phase, large and small internal friction peaks were observed with  $Q^{-1} \approx 1.3 \times 10^{-2}$  and  $8 \times 10^{-4}$ , respectively (fig.(a)). These two peaks were absent for the Al-Pd-Mn-Si 1/1-phase, which showed two other peaks instead. The Al-Pd-Mn-Si 2/1-phase exhibited the features of both the i- and 1/1-phases; it showed two peaks of the i-phase and one of the two peaks of the 1/1-phase (fig.(b)-(c)). All the observed peaks were of the thermally-activated relaxation type, and their activation enthalpies and frequency factors were evaluated. The larger peak of the i-phase, which was absent for the 1/1-phase and present with a much reduced intensity for the 2/1-phase, was shown to result from a relaxation process involving collective atomic motion. Collective and correlated phason jumps were discussed as a possible mechanism for it. Moreover, the peak was found in the Al-Cu-Fe i-phase, which was absent for the 1/1-phase in Al-Cu-Fe-Si system. It was speculated that the other peaks observed only for the approximant phases are due to Zener relaxations by the reorientation of atom pairs involving Si.

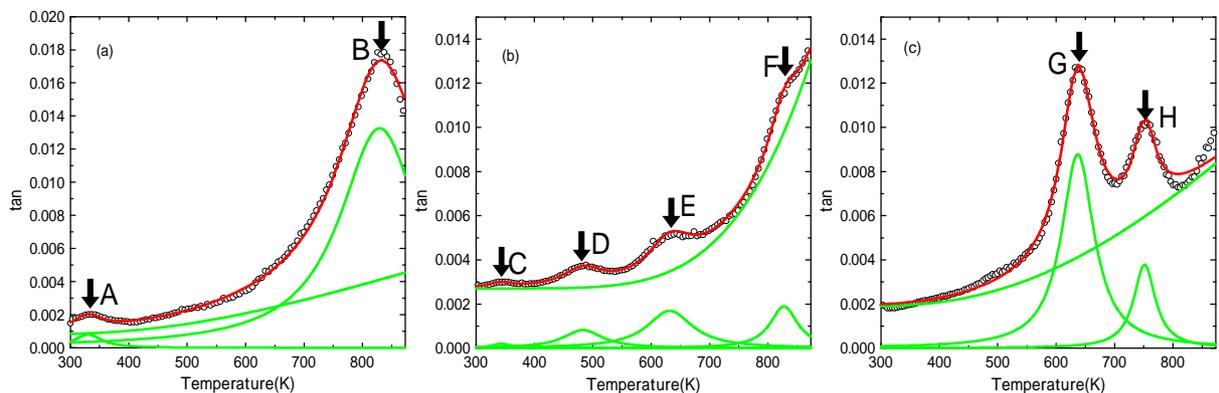


Fig. temperature dependences of the internal friction for the poly-grained samples of i-Al-Pd-Mn (a), and the 2/1- (b) and 1/1- (c) approximant phases in the Al-Pd-Mn-Si system at a frequency of 0.1 Hz. Open circles represent the experimental data. Red and green curves represent the results of the fitting; the red curves indicate the sum of the HTDB component and the Lorentz functions representing the peaks, and the green curves indicate the individual components.

## ON NATURE OF THE EXCESS HEAT CAPACITY IN THE ICOSAHEDRAL QUASICRYSTALS

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We present the experimental evidences indicating that the excess heat capacity ( $C_{ex}$ ) relative to the Debye model in the  $Al_{63}Cu_{25}Fe_{12}$  icosahedral phase contains the contributions associated with an inconstancy of a charge carrier concentration.

As is well known, i-phases display the  $C_{ex}$  contributions in the ranges both of moderate (20-300 K) [1] and high (700-1080 K) [2] temperatures. Among the possible reasons of these anomalies, the thermally excited phasons are supposed to be preferable, because the electron contribution being taken into account as  $\gamma T$ , where  $\gamma$  is the Sommerfeld coefficient, is negligible. Such a calculation of the electronic heat capacity is based on the assumption of a constant electron concentration in the system. The stable icosahedral phases are not alike. In particular, the concentration of charge carriers in the phase  $Al_{63}Cu_{25}Fe_{12}$  increases from  $\sim 10^{20} \text{ cm}^{-3}$  up to  $\sim 5 \times 10^{22} \text{ cm}^{-3}$  in the interval of 4.2 – 1000 K. The responses linear in these changes are the increase in conductivity  $\Delta\sigma$  and in paramagnetic susceptibility  $\Delta\chi$ . [3]. If the heat capacity of i-phases contains the electron contribution associated with an inconstancy of a charge carrier concentration then the internal energy of a system should display an increase  $\Delta U$  linear to the concentration change and so coordinated with  $\Delta\sigma$  and  $\Delta\chi$  magnitudes. Forming-up data necessary for the examination of the idea have been published in [4,5] for high temperature range and in [6] for moderate temperature range. Here we first represent and discuss the generalized result of the investigations, Fig. 1.

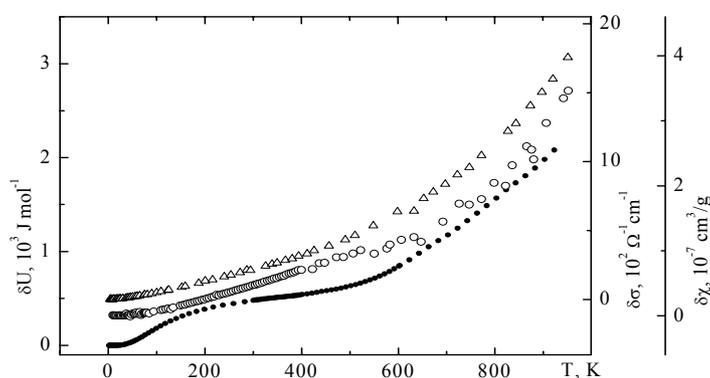


Fig.1 Correlations between the magnitudes which are linear in a number of thermally induced charge carriers:  $\delta U$  (●),  $\delta\sigma$  (Δ),  $\delta\chi$  (○).

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**EFFECT OF Ti ADDITION ON THE QUASICRYSTALLINE PHASE  
FORMATION AND INDENTATION CHARACTERISTICS OF  
Zr<sub>69.5</sub>Al<sub>7.5</sub>Cu<sub>12</sub>Ni<sub>11</sub> ALLOY**

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In recent years lot of attention has been given to Zr-based glassy alloys and their composite forms due to their high hardness, low coefficient of sliding friction, low adhesion, excellent wear resistance, high corrosion resistance, hydrogen storage properties etc. The minor alloying addition in Zr-based glassy alloys greatly influences their thermal and mechanical properties. This study deals with the crystallization behaviour and indentation characteristics of melt-spun (Zr<sub>69.5</sub>Al<sub>7.5</sub>Cu<sub>12</sub>Ni<sub>11</sub>)<sub>100-x</sub>Ti<sub>x</sub> (x=0-16; in at %) metallic glasses. The samples were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and Vickers microhardness tester. The addition of Ti for x>8 destabilizes the amorphous nature of Zr<sub>69.5</sub>Al<sub>7.5</sub>Cu<sub>12</sub>Ni<sub>11</sub> alloy. The DSC traces showed changes in crystallization behaviour with addition of Ti. Formation of a nano-quasicrystalline phase by annealing the glass has been found only upto x=12. Further increase of Ti content gives rise to formation of Zr<sub>2</sub>Ni type crystalline phase. In addition to this, the substitution of Ti influences the size of nano-quasicrystals. The size of nanoquasicrystals decreases with increasing addition of Ti. The load dependent hardness behaviour of metallic glasses and nanoquasicrystal-glass composites are reported in detail. The value of yield strength of the materials was estimated with the help of hardness values based on the empirical correlations available in literature. The formation of shear bands around the indentation periphery has been investigated with the help of scanning electron microscope (SEM). It has been observed that microstructural and morphological changes alter the indentation characteristics of Zr-Al-Cu-Ni alloys.

**SLOW DYNAMICS OF SPIN GLASS PHASES  
IN TSAI-TYPE Zn-Fe-Sc AND Zn-Mn-Sc QUASICRYSTALS**

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We studied the properties of spin freezing in Zn-Fe-Sc and Zn-Mn-Sc icosahedral quasicrystals (*i*-QCs) by the measurement of thermoremanent dc magnetization (TRM) time decay in order to find their class of spin glass. The Zn-Fe-Sc *i*-QC is the first case of significant magnetism arising from 3*d* transition metal Fe in *i*-QCs. The effective magnetic moments of each Fe (Mn) were estimated at 3.7  $\mu_B$  (0.31  $\mu_B$ ) from Curie-Weiss fits [1]. Edagawa *et al.* mentioned a prospect for Fe sites in the *i*-QC from results of  $^{57}\text{Fe}$  Mössbauer spectroscopy [2]. However, it is still obscure whether the Zn-Fe-Sc spin glass stems from geometrically (quasiperiodic) frustration or randomness because the detailed crystal structure analysis has not been carried out.

In QCs containing magnetic elements, the geometrical frustration may happen among spins because of a quasiperiodic structure. In the case of the Al-Pd-Mn *i*-QCs, only fraction (typically less than 1%) of Mn atoms shows local magnetic moments. Therefore the Al-Pd-Mn can be considered as canonical spin glasses in dilute magnetic alloys. On the other hand, in the Zn(Cd)-Mg-*R* (*R* = Tb, Ho, etc.) *i*-QCs, all of *R* atoms possess well-localized 4*f* magnetic moments and locate specific sites by a quasiperiodic manner. The *i*-QCs with rare-earth elements can be regarded as a geometrically frustrated spin system without randomness of the spins. In connection with this aspect, Dolinšek *et al.*, reported that the Zn(Cd)-Mg-*R* may be classified as a special class of spin glass between canonical spin glasses and superparamagnets due to the behavior of TRM time decay as a function of aging time  $t_w$  and cooling magnetic field  $H_{fc}$  [3].

In this study, we measured TRM of the  $\text{Zn}_{77}\text{Fe}_7\text{Sc}_{16}$  (annealed at 973 K for 20 h or 80 h) and the  $\text{Zn}_{75}\text{Mn}_{10}\text{Sc}_{15}$  (as-cast) by a dc SQUID magnetometer (Quantum Design MPMS-7). Measuring temperature  $T_m$  were 5 K and 10 K for the  $\text{Zn}_{77}\text{Fe}_7\text{Sc}_{16}$  (freezing temperature  $T_f = 7$  K) and the  $\text{Zn}_{75}\text{Mn}_{10}\text{Sc}_{15}$  ( $T_f = 14$  K), respectively.  $t_w$  were from 1 min to 5 h, and  $H_{fc}$  were from 20 Oe to 125 Oe. We have referred to Refs. [3] and [4] for the details of the experimental procedure. Both samples showed slowly decay of TRM as a stretched exponential function  $M_{\text{TRM}}/M_{fc} = \exp\{-(t/\tau_0)^\beta\}$  and the magnitude of the  $M_{\text{TRM}}/M_{fc}$  increased as  $t_w$  is extended. These results are consistent with the aging process where it takes long time to reach an internal equilibrium state of the spin system in an ultrametric organization of metastable state for spin glass phases. Regarding dependence on  $H_{fc}$ , the  $M_{\text{TRM}}/M_{fc}$  curves were decaying function with increasing  $H_{fc}$ . This relation between  $M_{\text{TRM}}/M_{fc}$  and  $H_{fc}$  are consistent with a model for the effect of a field change on dynamics of a typical canonical spin glass phase such as Cu-Mn [4]. Present results for the Zn-Fe(Mn)-Sc *i*-QCs are essentially different from that of the Zn(Cd)-Mg-*R* *i*-QCs with 4*f* moments in terms of classes of spin systems.

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## MAGNETIC PROPERTIES OF THE AG-IN-RARE-EARTH 1/1 APPROXIMANTS

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Since the discovery of quasicrystals, static and dynamical behavior of spins in quasiperiodic structure has been of particular interest. Theoretically, several quasiperiodic lattices with localized moments (spins) have been studied in details, and a number of intriguing magnetic orderings, including long-range quasiperiodic order, have been proposed to date. On the other hand, experimental investigation on existing magnetic quasicrystals always shows spin-glass-like freezing in the magnetic susceptibility measurements with considerably developed short-range antiferromagnetic correlations detected in the neutron scattering. Then, a natural question arises; why does the development of magnetic correlations terminate in the short-range order? There are two scenarios for the absence of the long-range order: i) the intrinsic quasiperiodicity may localize the spin correlations, or ii) the spin correlations only develop in the high-symmetry cluster, and the inter-cluster correlation may be randomized due to chemical or structural disorder commonly seen in quasicrystals and approximants. To draw a conclusion on this issue, it is worthwhile to study ordering behavior of magnetic approximants where, in a magnetic point of view, a high-symmetry clusters with localized magnetic moments forms a periodic crystal.

Then we have performed magnetic susceptibility and neutron scattering measurements on the Ag-In-RE (RE: rare-earth) 1/1 approximants. For most of the RE elements, the inverse susceptibility shows linear behavior in a wide temperature range, confirming well-localized isotropic moments for the RE<sup>3+</sup> ions. Exceptionally for the light RE elements, such as Ce and Pr, non-linear behavior was observed, possibly due to significant crystalline field splitting and/or valence fluctuation. For the RE=Tb approximant, we have performed detailed low-temperature magnetization and neutron-scattering measurements. The susceptibility measurement clearly shows a bifurcation of the field-cooled and zero-field-cooled susceptibility at  $T_f = 3.7$  K, suggesting a typical spin-glass-like freezing. On the other hand, neutron scattering detects significant development of short-range antiferromagnetic spin correlations in the elastic channel, as well as a broad peak at  $\hbar\omega = 4$  meV in the inelastic scattering spectrum. These features bear striking resemblance to those in the Zn-Mg-Tb quasicrystals, suggesting that the short-range spin correlations is due to local high-symmetry clusters commonly seen in both the systems.

## EELS AND SXES STUDIES OF ELECTRONIC STRUCTURES OF Zn-Mg-Zr ALLOYS

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After the discovery of quasicrystals, great effort has been spent for understanding the presence of quasiperiodic structured materials. Electron energy-loss spectroscopy (EELS) experiments of Al-based quasicrystals showed that Al L-edge spectra shows the presence of pseudogap structures and characteristic chemical shifts. The chemical shift indicated a decrease of valence electron charge at Al sites [1]. Recently, EELS and soft-X-ray emission spectroscopy (SXES) experiments on Al-Si-Mn alloys showed the chemical shifts in quasicrystalline phase exist not only for Al but also for Si sites [2]. Those imply an increase of covalency in quasicrystalline phase. MEM/Rietveld analysis of Al-Re-Si quasicrystalline alloys reported a covalent bonding nature [3]. Thus, it should be important to investigate the relation between a chemical shift and bonding nature of the quasicrystals not only for the Al-based ones but also for other quasicrystalline materials. In this study, the chemical shift of Zn-Mg-Zr alloys of primitive icosahedral quasicrystal (P-QC)  $Zn_{83.5}Mg_{9.5}Zr_7$ , face-centered icosahedral quasicrystal (F-QC)  $Zn_{75}Mg_{18}Zr_6$  and a 1/1-approximant of F-QC  $Zn_{77}Mg_{19}Zr_4$  phases were investigated. For Zn  $M_3$ -edge EELS measurements, a high energy-resolution EELS-TEM was used [4]. For Zn L-emission measurements, a SXES-TEM was used [5].

Figure shows Zn  $M_3$ -shell excitation spectra [Zn  $M_3$ -shell ( $3p \rightarrow CB(3d, 4s)$ )] of the P-QC and 1/1-approximant obtained with an energy resolution of 0.1eV. Lateral dashed lines are the background level. Spectral onsets of  $M_3$ -edge are indicated by arrows, which correspond to the Fermi level. It should be noted that the onset position of P-QC shows a shift to the larger binding energy side by 0.2-0.3eV compared with that of 1/1-approximant. Onset energy of Zn  $M_3$ -edge of F-QC showed a little shift to larger binding energy side by an order of 0.1eV compared with 1/1-approximant (not shown here). Those results show a presence of characteristic chemical shift in Zn-based quasicrystalline phase. Therefore, a chemical shift in quasicrystalline phases can be a common characteristic related to an increase of covalency in quasicrystal states. EELS and SXES on Mg and Zr will be also presented.

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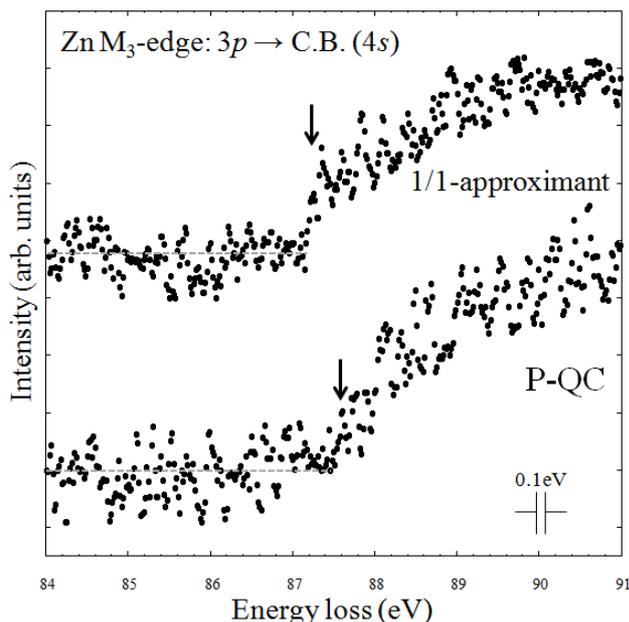


Figure: Zn  $M_3$ -shell excitation spectra of P-QC and 1/1-approximant.

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## ANOMALOUS CONDUCTION MECHANISMS OF INSULATING Al-Pd-Re QUASICRYSTALS

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The thermodynamically stable Al-based icosahedral quasicrystals have the anomalous electrical conductivities, such as semiconductor-like properties. Mayou et al. [1] proposed a possible explanation for the usual transport properties of quasicrystals in terms of hopping processes between wave functions mainly localized inside atomic clusters. One (I.K) of the present author [2-5] has considered the transport properties in the randomly distributed system of the correlated configuration (the aggregation), in which the nearest distance between each configuration, is  $\sim 2 / 2k_F$  (the quasicrystal-line system).

Akiyama et al. [6] have analyzed the electrical conductivity of metallic Al-Pd-Re quasicrystals in low temperature region close to the conduction mechanism of the quasicrystal-like system. Recent Kanazawa et al. [7] have analyzed electrical conductivities of metallic Al-Cu-Fe and Al-Cu-Ru quasicrystals in low temperature region due to the conducting mechanisms of the quasicrystal system. In addition, the present author [7,8] has discussed anomalous conduction mechanisms at stable Al-based quasicrystals from the stand-point of Wegner formula [9].

In this study, we will analyze the electrical conducting of the insulating Al-Pd-Re conductivities in the intermediate temperature-region without the variable range hopping region, taking into account the formula by Wegner [9].

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## Anisotropic Hall effect in single crystals of $\text{Al}_{13}\text{TM}_4$ and $\text{Al}_{13}(\text{Fe},\text{Ni})_4$ decagonal approximants

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The Hall effect in  $m\text{-Al}_{13}\text{Fe}_4$  and  $m\text{-Al}_{13}(\text{Fe},\text{Ni})_4$  ( $\text{Al}_{77}\text{Fe}_{21}\text{Ni}_2$ ) single crystals has been measured for all combinations of the electrical current and magnetic field directions, and in the temperature interval from 90 to 370 K.  $m\text{-Al}_{13}(\text{Fe},\text{Ni})_4$  is a ternary extension of  $m\text{-Al}_{13}\text{Fe}_4$  and therefore they both belong to the  $\text{Al}_{13}\text{TM}_4$  group of approximants to the decagonal quasicrystals. In both intermetallics the Hall coefficient  $R_H$  exhibits, as in decagonal quasicrystals, well defined anisotropy. However, in  $m\text{-Al}_{13}\text{Fe}_4$  compound  $R_H$  exhibits, in addition to the very large values (up to  $7 \cdot 10^{-9} \text{ m}^3\text{C}^{-1}$ ) at the lower temperatures, unexpectedly large temperature dependence and, for one of the magnetic field directions, the change of the sign from positive to negative value with the increase of temperature. These results are well interpreted within a simple two-band model if anisotropic electron and hole masses and anisotropic scattering times are taken into account. On the other hand, in  $m\text{-Al}_{77}\text{Fe}_{21}\text{Ni}_2$   $R_H$  exhibits a weaker temperature dependence and its anisotropy is well correlated to the anisotropy in crystalline  $o\text{-Al}_{13}\text{Co}_4$  and  $\text{Y-Al-Ni-Co}$  decagonal approximants and, therefore, to the anisotropy in  $d\text{-Al-Ni-Co}$  and  $d\text{-Al-Cu-Co}$  quasicrystals. The magnitudes and observed temperature dependence of anisotropic  $R_H$  in  $m\text{-Al}_{77}\text{Fe}_{21}\text{Ni}_2$  can be reproduced with similar anisotropic electron and hole masses as for  $m\text{-Al}_{13}\text{Fe}_4$  but with significantly greater residual scattering times. Large sensitivity of the transport properties on the alloy composition makes  $\text{Al}_{13}(\text{Fe},\text{Ni})_4$  a promising candidates for the investigation of the role of order *versus* disorder on the electronic properties of complex metallic alloys.

## Electrical properties of Al-Pd-Re quasicrystals prepared by spark plasma sintering method

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An icosahedral Al-Pd-Re quasicrystal has been known to exhibit insulating properties at low temperatures ( $\rho_{300K} \approx 16000 \mu\Omega\text{cm}$ ,  $\rho_{4.2K}/\rho_{300K} > 70$ ) [1] ) at a specific alloy composition of  $\text{Al}_{70.5}\text{Pd}_{21.0}\text{Re}_{8.5}$  [2]. In this study, in order to investigate the composition dependence of the electrical resistivity of Al-Pd-Re quasicrystals, we have incorporated spark plasma sintering method in the sample preparation, since it allows us to control the alloy composition with high precision.

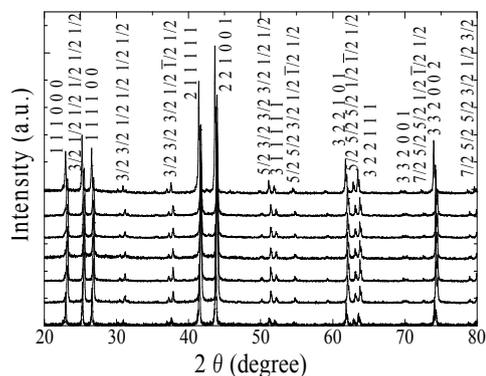
$\text{Al}_{70.5}\text{Pd}_{29.5-x}\text{Re}_x$  ( $x=8.0, 8.3 - 8.7, 9.0$ ) mother ingots were prepared by the SPS method using high-purity elements. Then, they were annealed at 923K for 48h under Ar atmosphere and quenched in water. Phase purity of the samples was examined by powder X-ray diffraction and the electrical resistivity was measured by a four probe method in a temperature range between 16 and 290K.

X-ray diffraction patterns (Fig1) reveal that all the peaks are sharp and can be indexed as the icosahedral QC, showing that a highly-ordered single phase of Al-Pd-Re i-QC was obtained. Electrical resistivities of  $\text{Al}_{70.5}\text{Pd}_{29.5-x}\text{Re}_x$  ( $x=8.0, 8.3 \sim 8.7, 9.0$ ) (Fig2) are very high with strong negative TCRs, and the highest resistivity is found to occur at 8.5at%Re.

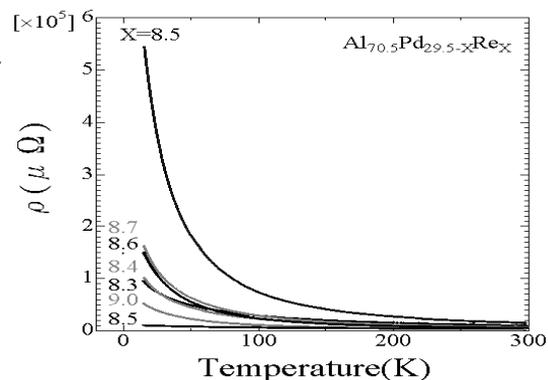
The present results can be understood by the shift of the Fermi level( $E_F$ ) via the variation of the  $e/a$  (electron per atom) value.  $E_F$  is presumably located at the bottom of the gap at 8.5at%Re. Results of other physical properties such as specific heat as well as of composition analyses will be presented.

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**Fig1.** The x-ray diffraction patterns of  $\text{Al}_{70.5}\text{Pd}_{29.5-x}\text{Re}_x$  ( $x=8.0, 8.3-8.7, 9.0$ ) quasicrystals.



**Fig2.** The electrical resistivity of  $\text{Al}_{70.5}\text{Pd}_{29.5-x}\text{Re}_x$  ( $x=8.0, 8.3-8.7, 9.0$ ) quasicrystals.

## Influence of heat treatment on the electrical resistivity of Al-Pd-Re quasicrystal

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### Introduction

Al-Pd-Re quasicrystal exhibits the highest electrical resistivity among all the icosahedral phases investigated up to date, and its electrical resistivity is very sensitive to the alloy composition. In general, arc-melted and subsequently annealed Al-Pd-Re icosahedral quasicrystals are highly porous and preparation of homogeneous samples is difficult by conventional preparation techniques. In this work, we have synthesized homogeneous full-density Al-Pd-Re quasicrystals by spark plasma sintering (SPS) method and the origin of the insulating properties, in particular, its dependence on the heat treatment conditions has been investigated.

### Experimental

Al<sub>70.5</sub>Pd<sub>21.0</sub>Re<sub>8.5</sub> mother ingots were prepared by the SPS method at 1123K for 30min. Then, the ingots were enclosed in a quartz tube under a purified argon atmosphere, and water-quenched after heat treatment at 923K for 48h(denoted as Sample A). For some alloys, we performed additional heat treatment at 923K(Sample B), 1023K(Sample C), 1123K(Sample D) for 48h. Electrical resistivity measurements were performed by a four probe method in a temperature range between 16K and 280K.

### Results and discussion

Figure 1 shows temperature dependences of the resistivity ratio ( $\rho/\rho_{280K}$ ) of Al-Pd-Re quasicrystal prepared in different annealing conditions.  $\rho_{280K} \approx 7000 \mu\Omega\text{cm}$  for all the samples and exhibit  $\rho_{16K}/\rho_{280K} \approx 12.0, 16.9(923\text{K}), 17.5(1023\text{K}),$  and  $17.7(1123\text{K})$ , for the samples A, B, C and D, respectively. Thus, the electric resistivity ratio is found to increase by the additional annealing. We note that the dependence on the annealing temperature is not strong but show a slight increase by increasing annealing temperature. Results on other compositions will be also discussed in the presentation.

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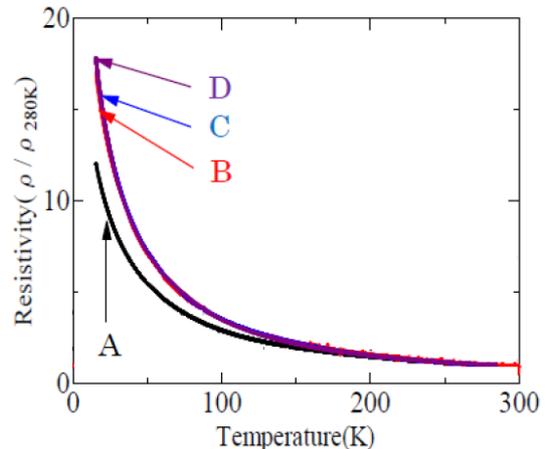


Fig. 1 Electrical resistivities of the Al<sub>70.5</sub>Pd<sub>21.0</sub>Re<sub>8.5</sub> quasicrystals by the SPS method

## Structural and physical properties of single-grained $\text{Cd}_6\text{M}$ 1/1 approximants

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$\text{Cd}_6\text{M}$  ( $\text{M} = \text{Ca}$ , rare earth elements) 1/1 approximants are composed of Tsai-type clusters located at the bcc lattice points. These alloys are known to exhibit a phase transition at a low temperature, which is interpreted to be of an order-disorder type and the  $\text{Cd}_4$  tetrahedron at the center of the Tsai-type cluster is ordered below  $T_c$  [1]. Besides the phase transition phenomena, it is also of interest to obtain insight into the behavior of  $4f$  magnetic moments sitting at the vertices of the  $\text{M}_{12}$  icosahedron. For investigations of the physical properties, especially the magnetic properties, of the  $\text{Cd}_6\text{M}$  approximants, it is preferable to prepare single-grained samples since they are free of imperfections such as foreign phases, grain boundaries, etc. Moreover, it has been reported in  $\text{Zn}_6\text{Sc}$  that highly ordered samples possess high  $T_c$  and exhibit a pronounced anomaly at the phase transition[2]. Therefore, it is also necessary to perform appropriate heat treatment on single-grained samples in order to elucidate the peculiar physical properties of the  $\text{Cd}_6\text{M}$  approximants.

In this work, we have prepared  $\text{Cd}_6\text{M}$  single crystals with high structural perfection by Self-Flux growth method (Melting temperature 993K / Cooling ratio -2K/h) followed by long-time annealing. Structural perfection of the samples was probed by electrical resistivity and heat capacity measurements. For a physical property, magnetic susceptibility measurements were performed in a temperature range between 2 and 300 K.

From the electrical resistivity measurements, an anomaly due to the order-disorder transition is found to become clearer when single grains were given additional annealing.  $T_c$  has also been found to increase appreciably by the heat treatment. Furthermore, a salient resistivity maximum appears around 20 K for  $\text{Cd}_6\text{Gd}$  and  $\text{Cd}_6\text{Tb}$  by annealing, implying an occurrence of another phase transition. Both the sharp transitions observed in the well-annealed single grain are understood as a result of reduction of atomic vacancies.

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## VARIABLE-RANGE HOPPING CONDUCTIVITY IN ICOSAHEDRAL QUASICRYSTALS

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An observation of the variable-range hopping electrical conductivity in icosahedral quasicrystals has been a subject of discussions for some time [1–3]. The regime of the variable-range hopping both of the Efros–Shklovskii type and of the Mott type has only been observed in poly-grain samples of icosahedral Al-Pd-Re with the resistivity ratio  $R = \rho(4.2 \text{ K}) / \rho(300 \text{ K})$  in the excess of about 10 and, surprisingly, often with nonzero electrical conductivity at zero temperature. The variable-range hopping regime has not been identified in the  $\sigma(T)$  curves measured on any other icosahedral phase including the single grains of icosahedral Al-Pd-Re. Poly-grain icosahedral Al-Pd-Re is a porous material that contains precipitations of a secondary phase [4], which has led to a discussion on the extrinsic nature of the variable-range hopping conductivity. Recently we have proposed an explanation of the variable-range hopping conductivity of poly-grain samples of icosahedral Al-Pd-Re based on an analogy with granular conductors [5]. The electrical conductivity of this model is determined by an intergranular tunneling and by the electrostatic energy. Depending on the barriers type, two regimes are possible — the metallic regime, typical for homogeneously disordered conductors, and the insulating regime of the variable-range hopping either of the Efros–Shklovskii type or of the Mott type. In the metallic regime the power-law temperature variation of the electrical conductivity with a small exponent leads to the logarithmic variation that is not observed in quasicrystals — correspondingly, the quantum interference corrections are most probable.

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## HYDROGEN IN THE 1/1 APPROXIMANT OF THE i-TiZrHf QUASICRYSTAL: ENERGY, BOND ORDER AND DIFFUSION

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Based on the density functional theory and ab initio pseudopotentials, using the structure of 1/1 approximant of icosahedral TiZrNi quasicrystal with replaced atoms Ni by Hf we have obtained the hydrogen solution energy for a number of possible interstitial (tetrahedral) positions in the 1/1 approximant of icosahedral TiZrHf quasicrystal. The structure was relaxed as well as the hydrogen positions.

Calculated charge state of atoms in the approximant under consideration for a wide range of the hydrogen-to-metal ratio (H/M) show that the hydrogen become more uncharged at highest H/M-ratio. We have also calculated bonding between hydrogen-metal, metal-metal and hydrogen-hydrogen atoms in terms of Mayer's bond order. This reveals that hydrogen-hydrogen and hydrogen-metal bonds are much less than metal-metal bonds.

Room temperature diffusion coefficient was estimated by Einstein-Smolukhovsky formula using data obtained from ab initio Car-Parrinello molecular dynamic. Activation energy of diffusion of single hydrogen atom has been evaluated from energy barrier profile, which arises when the hydrogen atom moves from one to other tetrahedral position.

## RENORMALIZATION PLUS CONVOLUTION APPROACH TO THE QUASIPERIODIC SYSTEMS WITH DEFECTS

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Based on the Kubo-Greenwood formula, we investigate the impurity effects on the *dc* and *ac* electrical conductance of quasiperiodic lattices by means of a renormalization plus convolution method [1]. This method combines the convolution technique with the real-space renormalization method, being able to address multidimensional quasiperiodic systems with defects. In this work, we report a detailed analysis of the electronic transport in Fibonacci systems with different kind of impurities. Both numerical and analytical results show the existence of transparent states in the *dc* conductivity spectra even for quasiperiodic systems with phasons [2]. Moreover, the introduction of local site or bond impurities induces resonant states, whose *ac* conductivity could improve that of ballistic systems. Finally, the effects of Fano-Anderson impurities [3] on the electrical conductivity are also analyzed.

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## SMALL POLARON APPROACH TO THE ELECTRON-PHONON INTERACTION IN QUASIPERIODIC LATTICES

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In this work, the interaction between electron and phonon is explicitly considered in the study of electronic transport in quasiperiodic systems at finite temperatures. Starting from the Holstein Hamiltonian, the transport of electrons dressed by lattice vibrational waves is analyzed by means of the small polaron approach [1]. This approach has the advantage of being simple and able to combine with the Kubo-Greenwood formula in order to investigate the small-polaron transport. In particular, taking the advantage of a previously developed renormalization plus convolution method [2], we have calculated the electrical conductance of multidimensional macroscopic quasiperiodic lattices including the electron-phonon interaction. The results reveal both metallic and anomalous temperature dependences, as a consequence of the Fermi energy position in the fractal band structure. For the periodic case, there are analytical solutions and they show a uniformly decreasing temperature dependence, where the power-law exponent is a function of the system dimensionality. Finally, we also study the effects of electron-phonon interaction on the optical conductivity in periodic and quasiperiodic nanowires with defects [3].

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## THE ENERGY SPECTRA AND TRANSPORT IN APERIODIC SEQUENCES OF QUANTUM DOTS IN EXTERNAL ELECTRIC AND MAGNETIC FIELDS

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Quantum dots and aperiodic sequences of quantum dots are very perspective for optoelectronics and nanoelectronics. We investigate the energy spectra and transport of electronic and Excitonic excitations for one-dimensional aperiodic sequences of quantum dots. Different kinds of sequences: Fibonacci, Thue-Morse, Cantor, double-periodic sequences were studied. The influence of the external magnetic field and electric field to energy spectra and particle localization was considered. In contrast to aperiodic sequences of atoms, for aperiodic sequences of quantum dots influence of even rather small magnetic fields (with value about tenths of Tl) is appreciable, and effect of intermediate fields (about several Tl) is essential. . Influence of electrical field become considerable in fields about several V/cm. The increase of the external electric and the external magnetic field contributes to decrease of tunneling probability. Magnetic field increases localization of electrons and excitons in QD and leads to energy spectrum shifts. Effect of Coulomb blockade was estimated when electric and magnetic fields were applied to aperiodic sequences of quantum dots. The transmission coefficient was determined using the quasi-classical approximation. The effect of resonance tunneling of the excitations was studied. The localization occurs at the finite values of the perturbations in contrast to the periodic one-dimensional sequences.

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CANCELED

# FIRST PRINCIPLES INVESTIGATION OF ICOSAHEDRAL QUASICRYSTAL APPROXIMANTS

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In complex metallic alloys structures the cluster-based description is used and is generally considered to be very helpful for understanding the geometrical building principles and for identifying structures. The term "cluster" is used to describe the recurrent structural units, and does not necessarily imply that they do not differ in chemical bonding or stoichiometry depending on their atomic environment or that they are mechanically stable units [1,2]. Quasicrystals as well as their periodic approximants can be described with these clusters. The extend of the physical interactions in and between these clusters are still subject of discussion. Indirect measurements of the clusters, such as cleavage of quasicrystals and analysis of its surfaces [3,4] and crack simulations [5] with models based on geometrical interactions differ on the appearance of the surfaces.

For a better understanding of these inter- and intracluster interactions, quantum mechanical first principle calculations were performed, investigating the relative bonding behaviour of the bonds. The underlying first principles structure relaxations were performed using density functional theory (DFT) with the generalized gradient approximation together with the all-electron projector augmented wave method, as implemented in the VASP code.

Charge density, electron localization function, Bader charge analysis and projection of the density of states onto the orbitals were used to analyze the bonding types. Strained cell calculations have been performed to simulated crack initiation. Additionally, artificial surfaces and cracks were introduced to the structures. The systems based on 1/1 approximants of the icosahedral AlCuFe and AlMnPd phases have been investigated and compared.

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# Poster Session 5

## Surfaces

Tuesday, June 15, 2010



## Multiple cluster model of Al-Co-Ni Co-rich quasicrystal

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The structure of Al-Co-Ni Co-rich quasicrystal has been studied by scanning tunneling microscopy (STM) combined with high-angle annular detector dark-field scanning transmission electron microscopy (HAADF-STEM).

STM observation of the surface compositional dependence of Co and Ni for Al-Co-Ni Co-rich quasicrystal has identified the 0.47 nm Co cluster and the 0.29 nm Ni cluster, respectively. From the STM images of the clean Co-rich surface, it is concluded that multiple main clusters is essential to explain the structure. From these results, three main clusters are proposed for both A and B stacking layers. These clusters are partly based on the Hiraga model [1]. Moreover, we have identified that the three main clusters have a tendency to form a boat-type cluster. It is also identified that the boat-type cluster forms 4 different tiling patterns: 5 boats pentagon, 5 boats star-shape, 8 boats twin-star, 3 boats head-inside. We have also successfully applied the boat cluster to the HAADF-STEM image of W-(AlCoNi) crystalline approximant to successfully identify the atomic arrangement.

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**The two nanometer cluster of the Al-Cu-Co quasicrystal surface  
observed by STM**

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The structure of d-Al-Cu-Co quasicrystal has been investigated intensively by transmission electron microscopy [1-2] and X-ray structure analysis [3]. It was revealed that the structure of d-Al-Cu-Co quasicrystal could be explained by the quasiperiodic arrangement of the 2 nm cluster. On the other hand, the d-Al-Cu-Co quasicrystal surface has been examined by scanning tunneling microscopy (STM) [4]. So far, the 2 nm cluster is not found in the STM image, since the STM image is too complex to find out the 2 nm cluster.

We successfully obtained the high resolution STM images at two adjacent terraces. A five-fold cluster in the diameter of 0.8 nm was observed in the high resolution STM images. From the STM images, it was identified that the 0.8 nm clusters had the same orientation on one terrace and that these clusters had the opposite orientation on the adjacent terrace. The 0.8 nm cluster was considered to be a partial cluster of Hiraga model [5]. Thus, the 2 nm cluster on the surface was identified from the distribution of the 0.8 nm clusters in STM images. Most of the 2 nm clusters observed in the STM images were found to have broken symmetry.

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**THE TWOFOLD SURFACE OF DECAGONAL Al-Co-Cu:  
EFFECT OF NANODOMAINS ON ADHESION AND GROWTH OF Ag**

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The structure of the clean twofold surface of decagonal Al-Cu-Co exhibits three distinct types of terminations, based on STM and LEED observations [1]. These have been interpreted within the framework of a recent bulk structural model [2]. Two of these terminations are Al-rich (85-100 atomic %) and one is richer in the transition metals (40-50 atomic %). The clean surface contains different types of imperfections, including nanodomains within flat terraces, where the type of termination switches within the terrace. These nanodomains may be manifestations of surface or bulk phasons [1]. The growth mode of Ag films is very sensitive to the presence of these nanodomains, and in some cases the Ag morphology clearly reveals nanodomains that are otherwise hidden. Using STM, we show that the Ag layer grows smoothly on the Co/Cu-rich termination, and three-dimensionally on the Al-rich terminations. This experimental evidence is supported by DFT calculations of adhesion energies of Ag on low-index surfaces of *fcc* Al, Co, and Cu.

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## SURFACES OF IN-AG-YB QUASICRYSTAL AND 1/1 APPROXIMANT

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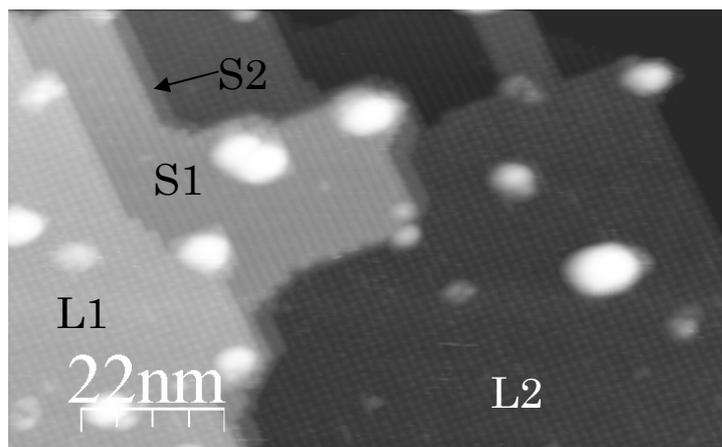
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We present STM studies on the high symmetry surfaces of i-In-Ag-Yb quasicrystal and the (100) surface of In-Ag-Yb 1/1 approximant. Step-terrace features and in-plane atomic arrangements are analyzed with using the refined structure model. For the 5-fold surface, it is found that both the step height distribution and the atomic arrangement are successfully explained by bulk termination at Yb-rich planes which intersect the cluster centers. This is also true for the 2-fold and 3-fold surfaces. Interestingly, these planes associated with the 2-fold surface have the maximum atomic density, but not those with the 5-fold and 3-fold surfaces. The 1/1 approximant exhibits a periodic step sequence along the [100] direction as expected. Large terraces appear with a periodicity of a half of lattice constant, suggesting that the termination also occurs at the planes intersecting the cluster center. However, the large terraces are always accompanied by two kinds of small terraces which appear in between the two adjacent large terraces. These features will be discussed on the basis of the cluster structure.



In-Ag-Yb 1/1 approximant (100) surface. Two kinds of small terraces (S1 & S2) appear in between the two adjacent large terraces (L1 & L2).

## CHARACTERISATION OF THE GROWTH OF Pb AND Bi THIN FILMS ON Ag-In-Yb QUASICRYSTAL USING XPS, UPS, STM AND LEED

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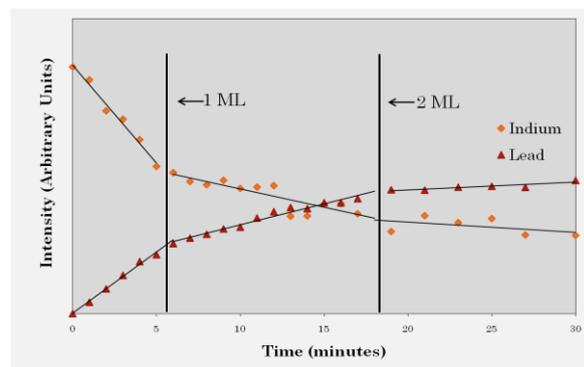
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The Pb thin film grown on the fivefold icosahedral Ag-In-Yb surface was found to be very promising model system for surface studies from various points of view [1]. Scanning tunnelling microscopy (STM) showed that quasicrystalline overlayers of Pb can be realized up to two atomic layers and after the completion of the quasicrystalline bilayer, periodic islands of selective heights are formed. Here we present the extended studies of this system using XPS, UPS and LEED.

Using XPS analysis to measure coverage as a function of dosage time there are clear, distinct changes in adsorption rates as coverage rises above 1ML and again above 2ML (Fig. 1). A similar scenario is seen for desorption of the Pb as a function of temperature. Annealing was done to a maximum of 420°C which also left a sub-monolayer stage which cannot be removed by annealing alone revealing the existence of surface sites where Pb is more tightly bound than others.

XPS data showed no shift in the binding energy peaks of the substrate at 1ML, 2ML or multilayer coverage indicating that Pb is weakly bound on the substrate, consistent with the desorption results. UPS data for corresponding stages show little change other than a sharpening of the Fermi edge as coverage is increased. Any possible quantum confinement effects were hidden by the dominance of the Yb 4f peaks close to the Fermi level. The Pb surface was found to have been to oxidation.

LEED data shows that both the mono and bi-layer coverages form pseudomorphic films whilst the multilayer coverage leads to the growth of islands with six fold rotation, consistent with STM data. These islands can form in any one of five possible orientations giving rise to a 30 spot LEED pattern.



**Fig. 1.** XPS intensities for Pb and In peaks as a function of dosage time

Initial studies of the growth of Bi on the same surface indicate the formation of a quasicrystalline overlayer. Further investigations of the system are being undertaken.

[1] H. R. Sharma, J. A. Smerdon, P. J. Nugent, M. Shimoda, H. Takakura, S. Ohhashi, A. P. Tsai, and R. McGrath

## GROWTH OF SB ON HIGH SYMMETRY SURFACES OF THE ICOSAHEDRAL AG-IN-YB QUASICRYSTAL

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The surface structure of the icosahedral (*i*) Ag-In-Yb quasicrystal, which has identical structure to the binary *i*-Cd-Yb [1], has been characterised using Scanning Tunneling Microscopy (STM) and the bulk model structure of *i*-Cd-Yb [2]. The availability of this surface has explored the possibility of using it as a template for the growth of atomic over layers. Here we demonstrate an example of Sb growth on high symmetry surfaces; 5-fold, 3-fold and 2-fold surfaces, studied by STM.

We have previously shown that the fivefold *i*-Ag-In-Yb surface terminates on atomically dense bulk planes which intersect the rhombic triacontahedral (RTH) clusters that make up the bulk solid. Here we will present several other features of step and terrace morphology and atomic structures such as Fibonacci like sequence observed at the step edges, and differing surface morphologies on the same terraces.

The deposition of a small amount of Sb on the surface enhances STM images at a positive bias voltage to the sample so that individual Yb atomic sites could be unambiguously resolved on the fivefold surface. Higher coverages yield pentagonal arrangements on the truncated RTH cluster centres which are only visible with a negative bias. At coverage's approaching one monolayer, the Sb atoms adopt a one-to-one bonding ratio with the Yb atoms of the substrate. As on the fivefold surface, the deposition of Sb on the 3-fold and 2-fold surfaces enhances the STM images. However, no ordered Sb overlayers were observed on these surfaces.

Investigation of adsorption properties of the Sb overlayer for molecules like C<sub>60</sub> is under progress. We will compare this result with the adsorption behaviour of the clean surface for the same molecules. We have found that the bonding strength between the substrate and C<sub>60</sub> is stronger than molecule-molecule bonding. However, the C<sub>60</sub> layer is found to be disordered.

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## STRUCTURE AND STABILITY OF Bi THIN FILMS ON THE FIVE-FOLD SURFACE OF THE ICOHSAHEDRAL Al-Pd-Mn QUASICRYSTAL

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Thin films of Bi deposited on the five-fold surface of icosahedral Al-Pd-Mn quasicrystal are found to form a quasiperiodic monolayer [1]. After completion of the monolayer crystalline islands of mostly even numbered layers grow with further depositions [2]. The results presented here -acquired with the techniques of Scanning Tunelling Microscopy (STM), Low Energy Electron Diffraction (LEED) and X-ray Photoelectron Spectroscopy (XPS),- elaborate the atomic structure and quantitative analysis of the stability of the overlayers.

Atomically resolved STM shows {012}-rhombohedral oriented Bi islands for a lower coverage of 4.1 monolayers. These islands proceed to transform to {0001}-hexagonal islands with further deposition. It is demonstrated that at a higher flux the density of rhombohedral islands increases and the transformation to a hexagonal orientation is inhibited. LEED obtained from the hexagonal structure islands evidences their rotational alignment along high symmetry directions of the substrate.

The thermodynamic stability of the thin film is quantified by heating and monitoring with XPS. It is found that the temperature for the thermal desorption of the multilayer (350°C) and monolayer (550°C) match well with earlier experimental studies [3]. Also, a more bound submonolayer coverage is evident. It is suggested that this coverage corresponds to the point at which saturation of the high surface energy nucleation sites occurs and the pure growth regime begins [4].

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## ELECTRON CONFINEMENT IN METAL THIN FILMS ON QUASICRYSTALLINE SUBSTRATES

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Quantum size effects affecting the growth of Bi as well as of Ag thin films were reported on several quasicrystalline surfaces [1,2]. Under specific growth conditions, islands with preferred thicknesses have been observed by scanning tunneling microscopy (STM) and were interpreted as a manifestation of electron confinement within the film thickness along the direction perpendicular to the surface plane. In the case of Ag thin films deposited on two different quasicrystalline substrates, the formation of quantum well states was observed by angle-resolved photoemission spectroscopy, thus confirming the electronic growth scenario [3]. It was suggested that the electronic confinement on quasicrystalline substrates is a consequence of incompatible point-group symmetry of the wave functions between the quasiperiodic substrate and the periodic film, rather than a consequence of the existence of the pseudogap at the Fermi energy. However, a recent STM study of an Ag thin film deposited on the fivefold surface of the icosahedral Al-Pd-Mn quasicrystal shows that the preferred 3-layer height islands actually consist of *nonfcc* structures, the first layer being pseudomorphic [4]. Thus, the origin of the confining barrier is not fully clear.

Here we will present new experimental results about both Ag and Bi thin films deposited on different complex substrates: the fivefold surface of the icosahedral Al-CuFe quasicrystal, the (100) surface of the orthorhombic Al<sub>13</sub>Co<sub>4</sub> and the (010) surface of the  $\xi'$ -AlPdMn approximants. The film morphology under specific deposition conditions is monitored by STM while the formation of quantum well states is investigated by photoemission spectroscopy for various film thicknesses. These experiments aim at a better understanding of the origin of the electron confinement on quasiperiodic surfaces.

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## SURFACE TERMINATIONS OF PERIODIC COMPLEX METALLIC ALLOYS: RELATIVE SURFACE ENERGY CALCULATIONS

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The surface energy is defined as the excess free energy at the surface of a material compared to the bulk. In a simple model, the surface energy is proportional to the number of missing bonds at the surface. This broken-bond rule accounts for the greater stability of the densest planes in the case of simple metals. More generally, the surface free energy minimization leads to the emergence of preferred surface orientations, and for a given (*hkl*) surface, interlayers relaxations and possible surface reconstructions. In metallic alloys, the introduction of different chemical elements offers additional mechanisms to minimize the surface energy, through a chemical surface segregation or by the selection of specific planes. In quasicrystals, the mechanism by which the surface energy is minimized is mainly the selection of dense Al-rich planes of the bulk structure, without any lateral reconstruction or chemical segregation [1].

While important, the surface energies are difficult to determine experimentally. Similarly, *ab initio* methods are able to calculate surface energies of metals [2] but in the case of complex metallic alloys, surface energy calculations are not so trivial: (i) the large number of atoms in the unit cell leads to a large number of atoms in the slabs used in the calculation, (ii) the different stoichiometries of the different atomic layers make generally impossible the direct comparison of the energy of a given slab with the corresponding bulk in order to derive the surface energy.

In this work, preferential surface terminations of some intermetallics chosen among quasicrystalline approximants and related complex metallic alloys are investigated by *ab initio* calculations [3]. Surface energies of different terminations are compared in order to determine the most stable ones that might form at the surface. These *ab initio* results are then compared to experiments based on scanning tunnelling microscopy, low-energy electron diffraction and X-ray photoemission. A parallel will be drawn with previous observations of terrace selection at quasicrystalline surfaces.

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## STRUCTURE OF THE (001) SURFACE OF THE $\text{Al}_9\text{Co}_2$ ALLOY

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Many quasicrystals have been discovered in the Al-rich aluminides, in parallel with a systematic study of related intermetallic compound like  $\text{Al}_3\text{Mn}$ ,  $\text{Al}_7\text{Cu}_2\text{Fe}$ ,  $\text{Al}_9\text{Co}_2$ ,  $\text{Al}_3\text{Ni}$  by Raynor and his collaborators [1]. A characteristic feature of the electronic structure of all these intermetallic compounds is the existence of a reduced density of state in the vicinity of the Fermi level. The origin of this pseudo-gap has been interpreted as the combined effect of the electron scattering by Bragg planes with sp-d hybridization [2,3].

Among these intermetallic compounds, the  $\text{Al}_9\text{Co}_2$  system presents an original centrosymmetric structure ( $P2_1/c$  space group) consisting of zig-zag alignments of single-capped square polyhedras formed by aluminium atoms surrounding a cobalt atom [4,5]. Attractive physical properties are likely linked to this specific crystal structure; in particular, surface properties are interesting for new technological applications such as heterogeneous catalysis.

In this study, the atomic and the electronic structure of the (001) clean surface of  $\text{Al}_9\text{Co}_2$  is investigated by a combination of (i) *ab initio* calculations based on the density-functional theory (DFT) and (ii) experimental surface analysis such as scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and x-ray photoelectron spectroscopy (XPS). Two different possible terminations, obtained from bulk truncation, are explored by DFT calculations: an aluminium rich top layer termination and a cobalt rich top layer termination, which is the densest atomic plane of the system. Interlayer relaxations, relative surface energies, DOS and simulated STM images are calculated to examine the stability and the electronic properties of these two possible surfaces. These results are compared to the experimental data in order to have an unambiguous description of the clean  $\text{Al}_9\text{Co}_2(001)$  surface termination.

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# THEORETICAL STUDIES ON CLEAN AND ADSORBED SURFACES of Ag-In-Yb

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Electronic structures of quasicrystal(QC)-related compounds are characterized by a pseudogap in the electronic density of states near the Fermi energy and semiconductor-like electronic properties are often observed. Such characteristic electronic structures also affect chemical properties and are expected to yield novel functions of QC surfaces. Extensive studies on clean and adsorbed surfaces of Al-based QCs have been done by many groups. Here we shall study surface electronic structures of a family of Cd-based QC, which shows unique contrast to the Al-based QCs. Since experimental data for surfaces of the Cd-based compounds are not available, we investigate Ag-In-Yb surfaces by first-principles electronic structure calculations. In a preliminary study for a slab of Ag-In-Ca 1/1 approximant, we found characteristic surface segregation, where Ag intrudes into the bulk and In extrudes to the vacuum [1]. We re-examine the segregation for Ag-In-Yb by using a slab model of 1/1 approximant carefully and discuss effects of the segregation on adsorption of other elements. For the five-fold surface of icosahedral Ag-In-Yb, experimentally observed flat terraces are analyzed as flat atomic planes with Yb-rich composition [2]. To simulate such surfaces, we adopt a cluster model extracted from the QC model by Takakura et al. [3] and study Pb adsorption onto Yb-rich surfaces.

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# Poster Session 6

## Applications

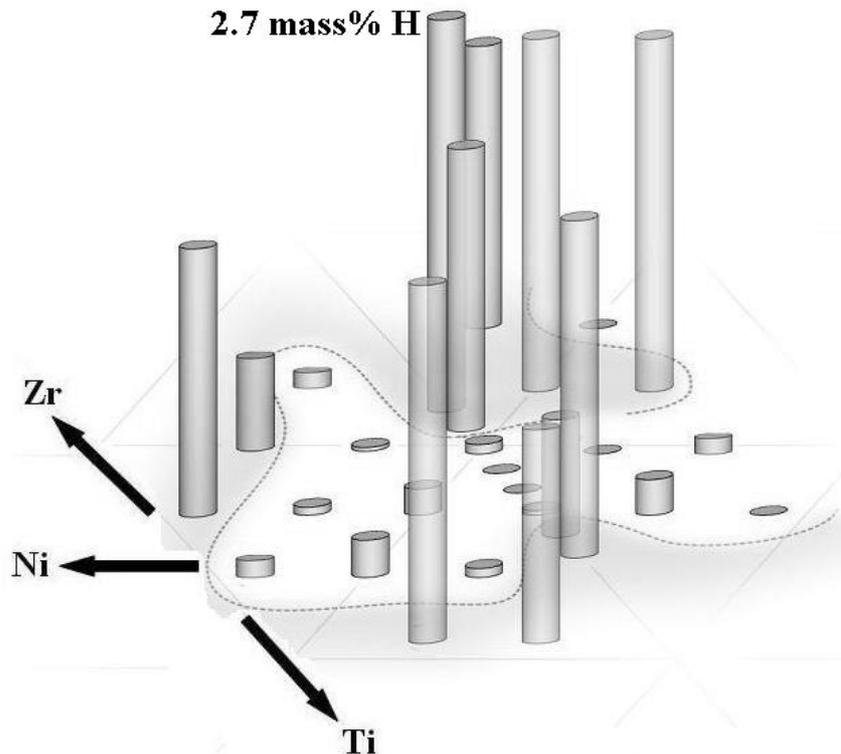
Tuesday, June 15, 2010



## SELECTIVE HYDROGENATION OF Ti-Zr-Ni ALLOYS

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We prepared series of Ti-Zr-Ni samples by melt-spinning and subsequent thermal treatment at 700°C for 2 hours in dynamic  $10^{-5}$  mbar vacuum in order to obtain crystalline mixture of C14 Laves and  $\alpha, \beta$ -(Ti, Zr) phases. These samples were exposed to technical (4.6) hydrogen gas at 300°C and 45 bar for 1000 min. The mass% of H was calculated from the sample weight difference before and after hydrogen desorption. We found relatively narrow area in Ti-Zr-Ni phase diagram, so-called zero-zone, where the hydrogen amount in crystalline samples varies between 0 and 0.3 mass%, *Figure*. At the border of this area H-content instantaneously increases to values from 0.8 up to 2.7 mass%, depending on the position in the phase diagram. Surprisingly, quasicrystalline (i-phase) samples show no selective hydrogenation and absorb over 1.3 mass% H in the interval of i-phase-forming compositions. XPS analysis revealed that the oxide layer thickness is similar after melt-spinning ( $\sim 11$  nm) and thermal treatment ( $\sim 3.5$  nm) for both type of samples, i.e. from inside and outside of the zero-zone. But the difference arises after hydrogenation, when the non-absorbing samples have 5-times thicker oxide layer, i.e. 50 nm.



**Figure:** Cut of the Ti-Zr-Ni ternary phase diagram with marked zero-zone, where the hydrogen absorption is either zero, negligible or below 0.3 mass% H. The composition between these crystalline samples varies for 3 at. %.

CANCELED

## PRESSURE-COMPOSITION-TEMPERATURE CURVES AND STRUCTURE STABILITY INDUCED BY HYDROGEN IN TiZrNi QUASICRYSTALS

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Ti-based quasicrystals have a large number of interstitial sites including tetrahedral and octahedral sites that are suitable for hydrogen uptake. The metastable  $\text{Ti}_{53-x}\text{Zr}_{27+x}\text{Ni}_{20}$  (where  $x=0, 4, 8$ ) quasicrystals were prepared by using a rapid quenching and the structure was determined by analyzing X-ray diffraction (XRD) patterns. To activate hydrogen absorption, the oxygen layer which prevents the hydrogen diffusion into the sample was eliminated by plasma etching in Ar atmosphere and subsequently a thin Pd coating was applied. The pressure-composition-temperature (P-c-T) curves of hydrogen in TiZrNi quasicrystals were measured in lower than 1000 Torr with a 0.001% resolution and in the temperature range of 200 ~ 300 C.

After the hydrogen absorption, no hint of hydride phase was found. The main peaks shift to the lower angle of two-theta in XRD patterns demonstrated that the quasi-lattice constants increased from 5.13 to 5.43Å after hydrogenation. The expansion of quasi-lattice constants was proportional with the total amount of absorbed hydrogen which was determined by measuring the sample mass after hydrogenation. Analyzing the full width at half maximum values of the main peaks in XRD patterns demonstrated that the coherence length significantly increased from 140 to 280Å after hydrogen absorption. No notable variation in peak shape was obtained from the annealed samples in vacuum. The P-c-T curves measured from  $\text{Ti}_{53-x}\text{Zr}_{27+x}\text{Ni}_{20}$  quasicrystals revealed that the pressure plateau of hydrogen was too low (lower than 1 Torr) for the practical application as hydrogen storage materials. Further studies are underway to increase the vapor pressure of hydrogen in TiZrNi quasicrystals and the foremost results will be presented. Also the analysis of morphologies and selected area diffraction (SAD) patterns measured from the hydrogenated and unhydrogenated TiZrNi quasicrystals will be discussed.

## HYDROGEN STORAGE CHARACTERISTICS OF TiVNi-QUASICRYSTAL COMPOSITE MATERIALS

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Hydrogen storage materials have attracted much attention in virtue of wide potential application. Especially, the metal hydride has been successfully used as negative electrode in the nickel-metal hydride (Ni-MH) secondary batteries due to their high hydrogen storage or discharge capacity is vital to practical application some extent. Ti-based icosahedral quasicrystal alloys contain great tetrahedral sites, and becomes one of the most promising hydrogen storage materials due to thermodynamical stability and exhibited good electrochemical hydrogen storage capacity. Several families of thermodynamically stable intermetallic compounds, such as AB<sub>3</sub> and AB<sub>5</sub>-type materials, have been largely investigated in order to be used as negative electrodes in Ni-MH hydride batteries. In fact, these alloys have a long life cycle, high rate capacity, excellent environmental compatibility and good charge-discharge kinetics. In this report, the research focus was put up electrochemical properties including the maximum discharge, the cyclic stability and the rate dischargeability for composition materials consist of TiVNi quasicrystal and AB<sub>3</sub> type composite materials.

## AL-CU-FE QUASICRYSTAL AS A CATALYST PRECURSOR FOR HYDROGEN PRODUCTION REACTION

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Quasicrystals (QCs) are unique form of matter that exhibit long-range order without periodicity and non-crystallographic rotational symmetries (i.e. 5-fold and 10-fold symmetries). Interest in QCs as catalyst arises from the unique properties that they offer: (1) brittleness, which allows them to be crushed to obtain fine particles; (2) a good composition, which includes a catalytic active element, such as Pd, Ni, or Cu. Recently, Al-Cu-Fe QC alloy powder leached in alkali aqueous solutions has showed high catalytic performance for hydrogen production by steam reforming of methanol (SRM:  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ) [1-3]. However, it is unclear as to how the QC works in the leaching process and catalytic activity. In this work, we examined the catalytic properties of SRM and cross-sectional observation with a transmission electron microscope (TEM) of Al-Cu-Fe QC catalyst prepared by NaOH leaching.

Figure shows TEM bright field images of the cross-section of fresh and spent (after SRM reaction) catalyst particles. The fresh QC catalyst (Fig. (a)) shows the formation of a homogeneous leached layer composed of Cu, Fe, and their oxides by leaching. Spent QC catalyst (Fig. (b)) showed no visible change in microstructure compared to fresh catalyst (Fig. (a)). This observation suggests that the QC catalyst has high stability under SRM reaction. On the other hand, for the fresh crystal ( $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_{10}$ ) catalyst (Fig. (c)), a complicated leached region was formed where Cu is enriched at the rim. A sintering of Cu particles drastically developed at the Cu enriched region under SRM reaction (Fig. (d)). TEM observation demonstrated that a higher dispersion of Cu was found for the QC catalyst than crystal catalyst. The high dispersion of Cu for the QC catalyst contributes high catalytic performance for SRM. We will discuss the catalytic performance in light of the microstructure and the dissolution behavior of Al during the leaching in our presentation.

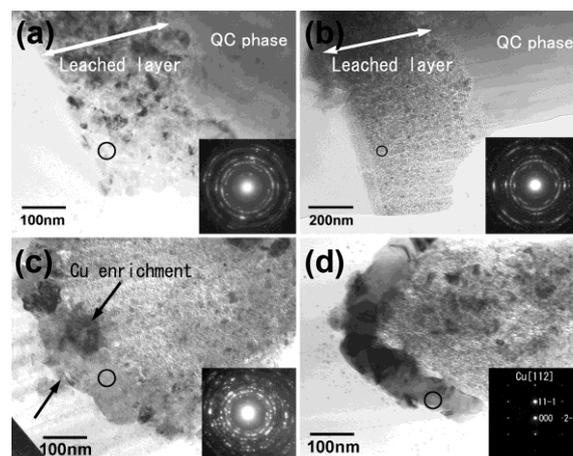


Figure TEM bright-field images of cross-section of QC ( $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ ) alloy catalyst (a) fresh and (b) spent, crystal alloy ( $\text{Al}_{70}\text{Cu}_{20}\text{Fe}_{10}$ ) catalyst (c) fresh and (d) spent.

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## SYNTHESIS OF CARBON NANOTUBES BY USING MECHANICAL-MILLED Al-Cu-Fe POWDERS AS CATALYSTS

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Quasicrystalline (QC) Al-Cu-Fe nanoclusters as a catalyst for the synthesis of carbon nanotubes (CNTs) have been studied as shown in the previous papers [1, 2]. It was shown that armchair-type (i.e., metallic) CNTs are preferentially synthesized by using Al-Cu-Fe ultrathin films (~3 nm in thickness) as a catalyst in catalytic-chemical vapor deposition (CVD) [1]. It was also shown that multi-walled CNTs were synthesized successfully by using *icosahedral* (*i*)-Al<sub>62.5</sub>Cu<sub>24.5</sub>Fe<sub>13</sub>, *i*-Al<sub>70</sub>Pd<sub>20</sub>Re<sub>10</sub>, and *decagonal*-Al<sub>70</sub>Ni<sub>15</sub>Co<sub>15</sub> bulk samples as catalysts [2]. It was suggested that QC nano-protrusions (~30 nm in diameter) at the surface of QC bulk samples have a significant catalytic activity for the synthesis of CNTs. The diameter of nano-protrusions seems to correlate with that of CNTs, ~30 nm in average diameter.

In this study, mechanical-milled Al-Cu-Fe powder samples were prepared for a catalyst in catalytic-CVD. Sample #1 was formed from an *icosahedral*-Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> as-cast ingot, as shown elsewhere [3], and sample #2 from an Al<sub>50</sub>Cu<sub>28</sub>Fe<sub>22</sub> with B2 phase. These powder suspensions dispersed by ultrasonication in ethanol were deposited and dried on silicon (100) substrates (10 mm squares and 0.5 mm thick). These samples were annealed at 723 K for 30 min in Ar ambient in a CVD reactor, followed by synthesizing CNTs at 923 K for 5 min by catalytic-CVD in ethanol, i.e., under similar conditions as described previously [2]. As a result, multi-walled CNTs, 20 nm to 30 nm in diameter, were obtained successfully by using both sample #1 and #2. In these cases, the crystallite size of these samples seems to correlate with the diameter of CNTs. It is suggested that mechanical-milled Al-Cu-Fe powders are useful for a catalyst in catalytic-CVD synthesis of MWNTs.

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## ANNEALING EFFECTS ON QUASICRYSTAL REINFORCED Mg-Zn-Zr EXTRUSIONS

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Quasicrystals (Qc) reinforced Mg alloys show good performance due to the well coherency between Qc and Mg matrix <sup>[1,2]</sup>. Rare earth (RE) metals are used widely to improve the mechanical properties of Mg alloys. However, RE are disadvantage at the cost and weight. With this in mind, we have studied Zn-Mg-Zr Qc <sup>[3]</sup> reinforced Mg extrusions which contains no RE metals. Improvement of the tensile strength at elevated temperature made by Qc particles has been achieved in the Mg-Zn-Zr extrusions. These extrusions have also shown randomized texture <sup>[4]</sup>. We report annealing effects on mechanical properties and microstructure for these extrusions.

The Zn-Mg-Zr Qc was prepared with induction furnace under Ar gas atmosphere. The nominal composition of Qc was  $Zn_{83.5}Mg_{11}Zr_{6.5}$ . Qc powder with grain size under 25  $\mu\text{m}$  and Mg powder with grain size around 150  $\mu\text{m}$  were blended and filled into a Cu billet. The fraction of Qc was 0-25 wt.%. The specimens were extruded with the reduction ratio of 15:1 and the ram speed of 10 mm/min at 350°C. Annealing treatment was performed at 300°C in air or 400°C under Ar gas for 0-200 hours. Micro structures and phase compositions were measured with electron probe micro analyzer (EPMA) equipped with wavelength dispersive spectrometer (WDS). Vickers hardness test and compression test were conducted at room temperature.

Qc grains dispersed homogeneously in the as extruded samples, which reacted with the Mg matrix at 300°C. The new phase formed at interface between Qc and Mg. Finally Qc grains transformed to Zn-Mg-Zr ternary phase and Zn-Mg binary phase at 400°C. Hardness of Mg-Zn-Zr extrusions decreased in both annealing conditions, but samples annealed at 400°C showed higher value than that at 300°C. Decrease in hardness by annealing might be come from the relaxation of strain induced by extrusion. Despite this strain relaxation, annealing at higher temperature could also produce some mechanical improvement.

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## A NOVEL QC (Al-Co-Ni)-POLYMER COMPOSITE FOR WEAR APPLICATION

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Efforts are made to prepare novel polymer (high density polyethylene)– quasicrystal (QC) particulate composite using compression molding technique. Low co-efficient of friction and high hardness of QC can be utilized to produce high strength and wear –resistant polymer composite. High density polyethylene (HDPE) is a linear thermoplastic polymer prepared from ethylene by a catalytic process. The Al-Ni-Co decagonal QC powders are used to prepare the composites. The QC particles from 5 to 20 wt% are loaded in the composite.

Densification studies indicate that it has been possible to obtain full dense composite at processing temperature of 130<sup>0</sup>C and holding time of 60 minutes (99.9% of theoretical density). X-ray diffraction analysis shows no interfacial reaction between the polymer and QC particles. Scanning electron microscopic studies reveal well dispersed nano-sized particles within the polymer matrix for all concentrations of the composite. The particles are found to be well bonded with the polymer. Wear studies shows reduced co-efficient of friction (0.2) and wear rate for composites. The composites with 20 wt% QC particles show best wear property.

# Poster Session 7

## New systems

Tuesday, June 15, 2010



## STRUCTURAL PHASE TRANSITION OF DENSE MONOLAYERS ON QUASIPERIODIC LIGHT POTENTIALS

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In comparison with crystals, quasicrystalline surfaces exhibit much larger structural and chemical complexity leading, for example, to unusual frictional, catalytical or optical properties. Deposition of thin films onto such surfaces can lead to novel structures which may exhibit unusual properties. Here we report a real space investigation of the phase behavior of micron-sized colloidal particles adsorbed onto a quasicrystalline decagonal and tetradecagonal substrates created by interfering five or seven laser beams. Different starting configurations, such as dense fluid and triangular crystals with different densities, are prepared. Our experiments show that the phase transition from a triangular crystalline structure to a decagonal quasiperiodic phase always occurs in two stages. First, rows of quadratic tiles are formed leading to a destruction of the local periodic ordering perpendicular to the rows. In the second stage, at a critical laser intensity, pentagonal tiles start to form and lead to a quasiperiodic ordering. For specific densities, at which the substrate-adsorbate interaction energy is minimized, the quadratic rows can be infinitely long. This leads to the formation of an archimedean-like tiling phase showing both crystalline and quasicrystalline structural properties.

CANCELED

# LIGHT TRANSMISSION THROUGH METALLIC-MEAN QUASIPERIODIC STACKS WITH OBLIQUE INCIDENCE

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The propagation of s- and p-polarized light through quasiperiodic multilayers is studied by the transfer matrix method. The stack consists of layers with different indices of refraction  $n_A$  and  $n_B$  which are aligned according to the inflation rule  $\mathcal{P} = \{B \rightarrow A, A \rightarrow ABA^{a-1}\}$  iterated  $m$  times starting with the symbol  $B$ . Here we focus on the transmission coefficient of the systems in dependency on the incidence angle and on the ratio of the indices of refraction  $u = n_A/n_B$ .

We obtain additional bands with almost complete transmission in the quasiperiodic systems at frequencies in the range of the photonic band gap of a system with a periodic alignment of the two materials, i.e.,  $ABAB \dots AB$ , for both types of light polarization. With increasing incidence angle these bands bend towards higher frequencies, and we derive a relation which indicates that for small and medium angles the bending is solely caused by the overall phase difference occurring during the passage of the stack. In particular, the curvature of the transmission bands in the quasiperiodic stack depends on the metallic mean  $\tau(a)$  of the construction rule, which relates the number  $f_A$  of layers  $A$  and the number  $f_B$  of layers  $B$  by  $\tau(a) = \lim_{m \rightarrow \infty} f_A/f_B$  in the limit of infinite system size. Additionally, in the quasiperiodic systems for p-polarized light the bands show almost complete transmission near the Brewster angle  $\vartheta_{\text{Br}}$  in contrast to the results for s-polarized light. Of course, for incidence angles  $\vartheta = \vartheta_{\text{Br}}$  one always obtains a transmission coefficient  $T = 1$  for p-polarized light.

Further, we present results for the influence of the indices of refraction at the midgap frequency of the periodic stack, where the quasiperiodicity was found to be most effective. While for small incidence angles transmission in a periodic system is only possible for values of  $u$  close to 1, in the considered quasiperiodic systems there is a whole range of possible ratios of indices of refraction  $u$  with almost complete transmission.



# Poster Session 8

## Related topics

Tuesday, June 15, 2010



CANCELED

## COEXISTENCE OF $\text{Mg}_4\text{Zn}_7$ AND $\text{MgZn}_2$ PHASES IN Mg-Zn-Y ALLOYS AND THEIR RELATIONSHIP TO QUASICRYSTALS

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Structure of rod-like Mg-Zn  $\beta'_1$  precipitates have been studied in Mg-Zn-Y alloys by high resolution transmission electron microscopy (HREM). The structure of these precipitates have long been believed to be based on  $\text{MgZn}_2$  structure, but were recently shown to have the structure of monoclinic phase  $\text{Mg}_4\text{Zn}_7$  with a complex domain structure. This phase is known to be structurally related to quasicrystalline phases. It has a layered structure perpendicular to  $[010]$  axis, with two similar main layers containing pentagonal coordinations rotated  $180^\circ$  to each other, and intermediate layers of zinc atoms which form vertices of icosahedral coordinations.

We show here that the structure of the  $\beta'_1$  precipitates consists of complex domains of  $\text{Mg}_4\text{Zn}_7$  and  $\text{MgZn}_2$  phases, with axial relationship  $[010]_{\text{Mg}_4\text{Zn}_7} \parallel \langle 11\bar{2}0 \rangle_{\text{MgZn}_2} \parallel [0001]_{\text{Mg}}$ . Both the phases consist of similar units of icosahedrally coordinated atoms. The structure of  $\text{MgZn}_2$  too can be considered a layered structure perpendicular to a  $\langle 11\bar{2}0 \rangle$  axis, the main layers containing pentagonal coordinations and intermediate layers of zinc atoms. Defect-like features in the  $\text{Mg}_4\text{Zn}_7$  phase form units of the  $\text{MgZn}_2$  structure. Two variants of the  $\text{MgZn}_2$  phase form in  $\text{Mg}_4\text{Zn}_7$ , mis-oriented with respect to each other by about  $72^\circ$ . One of these variants exhibits well known orientation relationship (OR) with the matrix  $\langle 11\bar{2}0 \rangle_{\text{MgZn}_2} \parallel [0001]_{\text{Mg}}$ ,  $(0001)_{\text{MgZn}_2} \parallel \{11\bar{2}0\}_{\text{Mg}}$ . In some regions, whole domains of the  $\text{MgZn}_2$  phase coexist with  $\text{Mg}_4\text{Zn}_7$ . A close examination of the structure revealed that alternate rows of zinc atoms perpendicular to the  $[0001]$  direction were replaced. Thus the structure of the  $\text{MgZn}_2$  phase is modified.

Layered structures and phenomenon of coexistence of two phases in nano-domains is similar to aluminum alloys such as in Al-Mn and Al-Mn-Cu, which imitate decagonal phase. The phenomenon observed here is its parallel in Zn-Mg-based alloys. The interplanar spacings along the common direction match the periodicity of the decagonal phase reported in Zn-Mg-based alloys.

## Stable configurations of atoms in $Mg_2Al_3$ phases

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The first description of the  $\beta$ - $Mg_2Al_3$  structure was provided by Samson in 1965 [1]. It is often referred to as the Samson phase. Because of its complexity and potential new technical applications, during the last few years the Samson structure aroused considerable interest among crystallographers [2].

Samson phase is a complex cubic structure with  $a = 2.8242(1)$  nm and it is decorated by 1168 atoms. Below  $214^\circ\text{C}$  the structure undergoes a transformation to the  $\beta'$ - $Mg_2Al_3$  which is a rhombohedral phase with  $a_r = 1.9968(1)$  nm,  $c_r = 4.89114(8)$  nm. Comparison of two different types of  $Mg_2Al_3$  structures: cubic  $\beta$  and rhombohedral  $\beta'$ , leads to the conclusion that all atoms of the Samson structure with SOF = 1 (site occupation factor) do not change their position during the phase transformation.

New description of the two phases is based on the rode-like domains which are mostly built from two structural units: C14 and C36 of the Laves phases. Domains are shifted with respect to each other by  $1/3$  of the main diagonal length of the cubic unit cell, and in a base plane they form a hexagonal superstructure with the modulation vector equal to  $3/22$  [3]. Such superstructure of domains together with the symmetry of individual domains are responsible for cubic or rhombohedral symmetry of an average complex unit cell.

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**IN SITU OBSERVATION OF AGEING PROCESS AND NEW ORIENTATION  
RELATIONSHIP OF CONTINUOUS PRECIPITATES IN  
MAGNESIUM-ALUMINIUM BASED ALLOYS**

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There has been an increasing interest on Mg-9wt%Al-1wt%Zn-0.2wt%Mn (AZ91) alloy among lightweight magnesium-based alloys, due to its application in the automotive, aerospace and electronic industries for its best combination of castability, mechanical strength and ductility. It was reported that the age-hardening response of AZ91 alloy is poor compared with many age-hardenable aluminum alloys, and this is due to the orientation relationship (OR) and morphology (particle size, shape, etc.) of the continuous precipitates. According to the Mg-Al binary alloy phase diagram, the precipitation phase in AZ91 is equilibrium phase  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> with a complex body centered cubic ( $\alpha$ Mn) structure. The  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase is a typical example of Frank-Kasper phase or so-called topologically close-packed phases. The lattice parameter for  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase is 1.05438nm (space group  $I\bar{4}3m$ ). The predominant fraction of continuous precipitates  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase is thin lath with the primary habit plane parallel to the basal plane of the matrix (0001)<sub>m</sub> and possesses the Burgers OR with the matrix. The second type of continuous precipitates with minor fraction, has the primary growth direction perpendicular to the basal plane (0001)<sub>m</sub> and has the Crawley OR, i.e. (0001)<sub>m</sub>//(111)<sub>γ</sub>, [11 $\bar{2}$ 0]<sub>m</sub>//[11 $\bar{2}$ ]<sub>γ</sub> or [ $\bar{1}$ 100]<sub>m</sub>//[ $\bar{1}$ 10]<sub>γ</sub>. The morphology of the Crawley OR precipitates was observed to be in the form of a hexagonal prism-shaped rod. The third type of the continuous precipitates possesses the OR in the form of (1 $\bar{2}$ 11)<sub>m</sub>//( $\bar{1}$ 10)<sub>γ</sub>, [10 $\bar{1}$ 0]<sub>m</sub>//[110]<sub>γ</sub>, denoted as the Porter OR, is even less frequent. The Porter OR precipitates have the primary growth direction lying at an angle of about 16° to the normal of the (0001)<sub>m</sub>. Only the minor fraction continuous precipitates (Crawley OR and Porter OR) act as barriers for dislocations to glide on the basal planes. Hence, the continuous precipitated particles with Crawley OR and Porter OR increase in volume fraction will contribute to improving the age-hardening response of the Mg-Al based alloys. In this study, the continuous precipitating process of Mg-Al based alloys and was observed in situ by TEM equipped with a heating stage for specimen, and some typical precipitated particles were analyzed by HRTEM. In addition to the thin plate-shaped continuous precipitates with Burgers OR, the  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase continuous precipitates in the form of the rod-shaped with Crawley OR and Porter OR were observed in situ and analyzed by TEM and HRTEM. During this study not only the continuous precipitates with the reported ORs were confirmed, but also a new OR of continuous precipitates, i.e. (0001)<sub>m</sub>//(110)<sub>γ</sub>, [10 $\bar{1}$ 0]<sub>m</sub>//[ $\bar{1}$ 13]<sub>γ</sub>, was observed in the Mg-Al based alloy. In addition, the stereographic projections of ten ORs including the new OR were calculated and discussed for Mg-Al based alloys.

## Structural relationships between hexagonal $\text{MgZn}_2$ , monoclinic $\text{Mg}_4\text{Zn}_7$ and related transition structures in Mg-Zn-Y alloys

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Intermetallic precipitates formed on deformation twin boundaries in heat-treated and aged Mg-Zn-Y alloys have been investigated via high-resolution transmission electron microscopy. These coarse spheroidal precipitates contained domains belonging to the  $\text{MgZn}_2$  hexagonal Laves phase as well as the monoclinic  $\text{Mg}_4\text{Zn}_7$  phase. Both phases are structurally related to the quasi-crystalline phase formed in Mg-Zn-Y alloys. The Laves phase is comprised of broad rhombohedral units with acute angle  $\sim 72^\circ$ , similar to those identified in the quasi-crystalline phase. The monoclinic phase contains a (differently-arranged) series of such rhombohedral units along with additional hexagonal prismatic units and has also been viewed as an approximant to decagonal quasi-crystalline structures.

The hexagonal  $\text{MgZn}_2$  and monoclinic  $\text{Mg}_4\text{Zn}_7$  phases co-existed as discrete domains within individual precipitates, with interfaces parallel to the (100) and (001) faces of the  $\text{Mg}_4\text{Zn}_7$  phase. A number of related transition structures were also identified at the interfaces between  $\text{MgZn}_2$  and  $\text{Mg}_4\text{Zn}_7$  phases. These transition structures consisted of the same broad rhombohedral and hexagonal units as the  $\text{Mg}_4\text{Zn}_7$  phase, but with differing numbers of rhombohedra separating the hexagonal units. This yielded several monoclinic structures with different compositions and lattice parameters from that of the  $\text{Mg}_4\text{Zn}_7$  phase.

The monoclinic  $\text{Mg}_4\text{Zn}_7$  phase, hexagonal Laves phase and monoclinic transition structures were all oriented so as to allow a continuous patterning of rhombohedral units across the interfaces. These results highlight the close structural similarities between the precipitates of the Mg-Zn-Y alloy system and the value of using approximants to better understand quasiperiodic structures.

## MICROSTRUCTURE AND MECHANICAL PROPERTIES OF A RAPIDLY SOLIDIFIED MG-9.0WT%AL-1.0WT%ZN-4.0WT%SN ALLOY

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As the lightest structural metal, magnesium based alloys are considered as suitable candidates for use in automotive industry. The most common types of these materials are those based on the Mg–Al system, such as the Mg–9wt%Al–1wt%Zn (AZ91) alloy for its best combination of castability, mechanical strength and ductility. Despite many advantages, these alloys have relatively poor mechanical properties at elevated temperatures, mainly due to the formation of the Mg<sub>17</sub>Al<sub>12</sub> discontinuous precipitates at the grain boundaries and continuous precipitates in the grain internal regions. According to the Mg–Al binary alloy phase diagram, the precipitation phase in AZ91 is equilibrium phase Mg<sub>17</sub>Al<sub>12</sub> with a complex body centered cubic ( $\alpha$ Mn) structure. Accordingly, attempts have been made to develop new magnesium–aluminum based alloys having improved structural stability at the high temperatures. Sn, as the major alloying element, is chosen due to its high solid solubility in the Mg matrix over a wide temperature range. It forms thermally more stable Mg<sub>2</sub>Sn phase with an antifluorite structure. The present study deals with the microstructure and mechanical properties of rapidly solidified ribbons of an Mg–9.0wt%Al–1.0wt%Zn–4.0wt%Sn alloy. The study has been carried out on rapidly solidified ribbons because this technique is a suitable way to produce fine-grained metastable microstructures (Figure 1) that could be optimized through a proper thermal treatment.

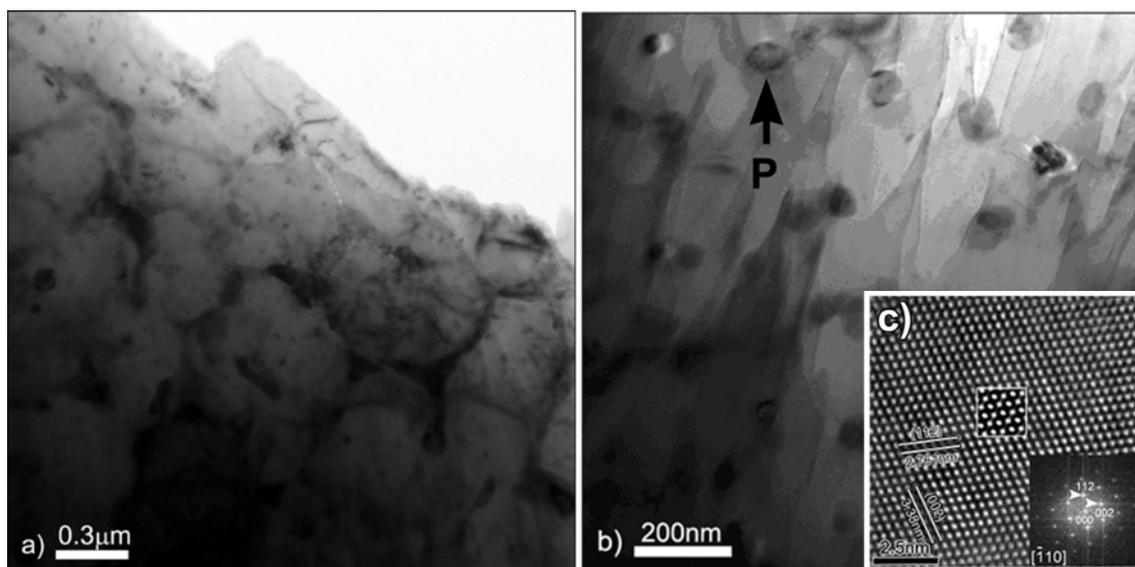


Figure 1 Micrographs showing the cellular dendritic structure of the Mg-9.0wt%Al-1.0wt%Zn-4.0wt%Sn alloy in the rapidly solidified condition. (a) bright field TEM image; (b) enlarged bright field TEM image; (c) HRTEM image of an Mg<sub>2</sub>Sn particle marked as P in (b).

## ELECTRONIC STRUCTURE OF $\text{Ag}_9\text{In}_4$ , $\text{Ag}_5\text{Zn}_8$ AND $\text{Mn}_3\text{In}$ GAMMA-BRASSES STUDIED BY FLAPW BAND CALCULATIONS

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There are more than 20 binary alloy systems, in which stable gamma-brasses containing nominally 52 atoms per unit cell with the space group  $I\bar{4}3m$  or  $P\bar{4}3m$  are formed, providing us with opportunities to study systematically the stabilization mechanism of such structurally complex metallic alloys. In the present work, we study the electronic structure of the  $\text{Ag}_9\text{In}_4$ ,  $\text{Ag}_5\text{Zn}_8$  and  $\text{Mn}_3\text{In}$  gamma-brasses with a particular attention to the pseudogap structure by means of the WIEN2k FLAPW-band calculations. The electronic densities of states (DOSs) derived for the three compounds are shown in Fig.1. A deep pseudogap is found across the Fermi level in both  $\text{Ag}_9\text{In}_4$  and  $\text{Ag}_5\text{Zn}_8$  gamma-brasses, being well consistent with the previous report on  $\text{Cu}_9\text{Al}_4$  and  $\text{Cu}_5\text{Zn}_8$  gamma-brasses [1]. However, the pseudogap is apparently hidden behind the large Mn-3d band in the  $\text{Mn}_3\text{In}$  gamma-brass. The origin of the pseudogap formed across the Fermi level is studied by making full use of the FLAPW-Fourier method.

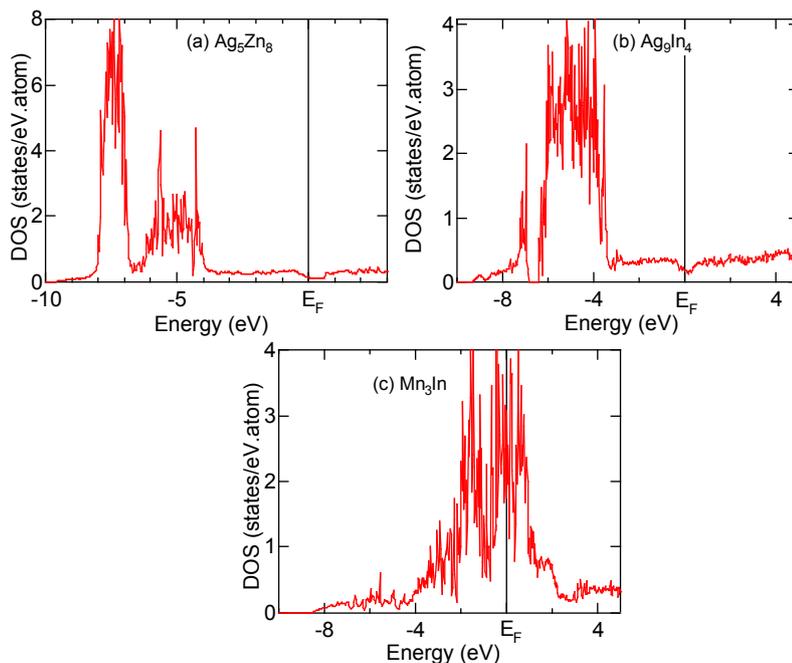


Figure 1. DOS for (a)  $\text{Ag}_5\text{Zn}_8$ , (b)  $\text{Ag}_9\text{In}_4$  and (c)  $\text{Mn}_3\text{In}$  gamma-brasses.

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## STRUCTURAL BUILDING PRINCIPLES OF COMPLEX INTERMETALLICS

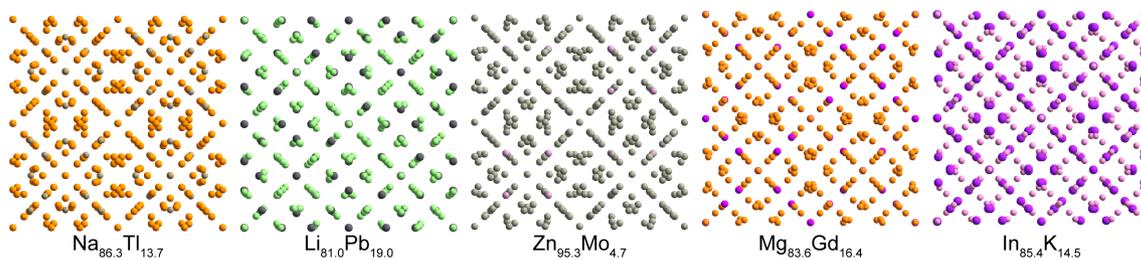
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A systematization of the structures of highly complex intermetallic phases is attempted as a long term goal within this work. Therefore we examined the structures of intermetallic compounds with huge unit cells, starting with a large group of cubic face-centered unit cells containing approximately 400 atoms. The studied structures crystallize in space groups symmetries  $F\bar{4}3m$  and  $Fd\bar{3}m$ ; unit cells of some examples are shown below (projected on the (001) plane).

The geometrical building principles of more than 30 structures are discussed by means of two different methods, *i.e.* the cluster approach and the modular approach. The former describes the structure as a packing of polyhedral clusters, which may consist of several cluster shells. The choice of clusters can be considered as justified when leading to a description of the structure which is as simple as possible. This mostly involves a high degree of transferability of a model to a different structure type, as well as highly symmetric polyhedra. By those means, the degree of complexity of a structural model may be reduced and underlying packing principles made intelligible. The modular approach constitutes crystal structures by structure modules, which are part of other structure types as well.

We start our investigations with structures described by the highest-symmetric lattice and thus described in cubic face-centered space groups. The chosen class of structures stands out in the multitude of intermetallics due to its quantity: only a small number of singular structures were found to exhibit bigger unit cells and it is a large enough group of structures to additionally substantiate the significance of a detailed study. All structures consist solely of pure metals, but nevertheless show a high diversity in their chemical composition. We discuss stabilizing forces in the investigated structures: thorough geometrical analysis and symmetry considerations are complemented by first-principles studies of the examined structures. Consequently, we hope to clarify the influences of packing principles and crystal-chemical driving forces on the building scheme of intermetallic structures.



STRUCTURAL ANALYSIS OF AMORPHOUS ZR<sub>70</sub>PD<sub>30</sub> ALLOY  
BY ANOMALOUS X-RAY SCATTERING COUPLED WITH REVERSE MONTE  
CARLO SIMULATION

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Amorphous materials exhibit the characteristic behaviors different from crystalline materials. This fundamental feature has encouraged us to perform a number of structural studies. Our group has developed anomalous X-ray Scattering (AXS) method in order to obtain the environmental structural information around constituent elements in amorphous materials. This environmental information should be included in the ordinary reverse Monte Carlo (RMC) analysis in order to obtain more reliable structural model. This paper reports the results of our new analytical approach of AXS-RMC for the structural analysis of a Zr<sub>70</sub>Pd<sub>30</sub> amorphous alloy. Crystallization of icosahedral phase by annealing has been reported for Zr-based amorphous alloys with noble metals [1-3]. The Zr<sub>70</sub>Pd<sub>30</sub> amorphous sample can be classified into this category and the characteristic crystallization was frequently attributed to the presence of icosahedral clusters [4].

AXS method is a powerful diffraction technique, which utilizes the energy dependence of atomic scattering factor at the X-ray absorption energy. The environmental structure around a specific element can be obtained by analyzing the differential intensity measures at the absorption edge. Since RMC method serves a 3-dimensional structural model, the combinatorial AXS-RMC analysis allows us to discuss the detailed structural information around every constituent element. Master ingot samples were prepared by the arc melting and ribbon samples were produced by the common single roller rapid quenching technique. AXS measurement was carried out at the synchrotron radiation (MISS, KEK, BL-7C, BL-NW10A).

Present AXS-RMC analysis has revealed the particular middle range ordering of the Pd-Pd pair together with the fundamental local structural units around Zr and Pd. Voronoi analysis indicates that the Pd-centered polyhedra with more than 8 pentagonal faces are common in the Zr<sub>70</sub>Pd<sub>30</sub> amorphous structure. Therefore, the fraction of such local structural units similar to Pd-Zr<sub>12</sub> icosahedra is suggested to be one of the important roles for the formation of the icosahedral phase by annealing.

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## STUDY OF PRECIPITATIONS IN Zr-Cu-Ni-Al-Nb BULK METALLIC GLASS MATRIX COMPOSITES CONTAINING QUASICRYSTALS AND CRYSTALS

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To enhance the understanding of the macroscopic mechanical properties, the corresponding detailed microstructure study of the Zr-Cu-Ni-Al-Nb bulk metallic glass matrix composites was conducted using transmission electron microscopy techniques after the mechanical testing and preliminary scanning electron microscopic observation. The major icosahedral quasicrystal phase precipitated in the alloys was determined to be primitive lattice with the quasilattice constant  $a_r = 0.54337$  nm. The misalignment of the systematic diffraction spots was broadly observed indicating the existence of the phason strain, which was also confirmed by the high resolution electron microscopy images. The displacements of the diffraction spots could be attributed to linear phason strain after the detailed measurement of the shifts, quantitative fitting and calculation. The twinning and domain structures of the quasicrystals and other crystal precipitates were also observed in the composites. The influence on the mechanical property of all the above-mentioned precipitates and microstructures including the existence of the phason strain were discussed then. The linear phason strain method was also used to consider the structural connection between the quasicrystal phase and the corresponding crystal precipitates, which may be the crystalline approximants of the quasicrystal.

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## RADIAL DISTRIBUTION FUNCTION ANALYSIS OF RANEY PD AND RH FINE PARTICLES

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Catalytic skeletal ultra-fine particles can be obtained by alkali-leaching of aluminum from alloy powders Al-X ( $X$ =Transition metals, precious metals) [1]. During the alkali-leaching process, crystal structures of parent alloys are decomposed and X-ray diffraction patterns of resultant particles are very broad and diffuse. These features could be generally attributed to small size of crystallite, lattice defects or rearrangement of atoms and those depend on its composition and reaction environment [2]. Further structural study is required in order to elucidate the leaching mechanism including rather complex liquid-solid reactions together with formation of skeletal surface morphology, which may serve their unique catalytic properties. In this study, structures of Raney Pd and Rh fine particles were analyzed by the high-energy X-ray diffraction.

Alloys of decagonal Al<sub>75</sub>Pd<sub>25</sub> and Al<sub>9</sub>Rh<sub>2</sub> with Al<sub>9</sub>Co<sub>2</sub>-type structure were reacted with 10 wt% NaOH aqueous solution at room temperature. Obtained fine particles were washed and dried at 50 °C. X-ray diffractions of the obtained fine particles were measured with synchrotron X-radiation at incident X-ray energy 28 keV at PF-AR-NW10A in Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK).

The radial distribution function (RDF) calculated from X-ray diffraction pattern for the fine particles obtained from decagonal Al<sub>75</sub>Pd<sub>25</sub>, indicates colorations corresponding to Pd-Pd correlations in *fcc*-Pd structure. RDF for leached Rh particles also indicates Rh-Rh pairs such found in *fcc*-Rh. These results indicate atomic rearrangement toward ordinary *fcc*-typed structure was occurred during the leaching.

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## Heterogenous equilibria and crystal structure of the $\Phi$ phase in the Al-Mg-Zn system

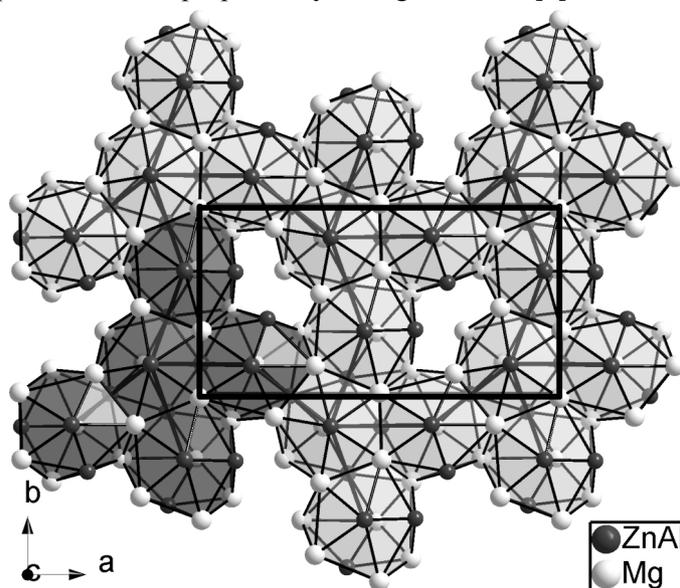
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The Al-Mg-Zn system contains four ternary intermetallic phases [1], called  $\tau_1$ ,  $\tau_2$ , q and  $\Phi$ .  $\tau_1$  and  $\tau_2$  are Bergman-type approximants of the quasicrystalline q phase. A structural model for the  $\Phi$  phase was first proposed by Bourgeois et al. [2] based on TEM investigations. Here, we report on the



heterogenous equilibria, the homogeneity range, the crystal and electronic structure of the  $\Phi$  phase. The crystal structure has been characterized by X-ray single crystal structure refinement at the composition  $\text{Al}_{27}\text{Mg}_{50}\text{Zn}_{23}$  (*oP*152, *Pca*2<sub>1</sub>,  $a = 16.812(2)$  Å,  $b = 8.937(3)$  Å,  $c = 19.586(4)$  Å). The Al and Zn atoms are all in icosahedral coordination. These icosahedra form structural units of broken fivefold symmetry arranged at the vertices of boat tiling, similar as found in decagonal quasicrystals.

**Figure 1.** Packing of (Al,Zn) centred icosahedra in the crystal structure of the  $\Phi$  phase in the Al-Mg-Zn system.

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