

# **Interdisciplinary Symposium for Quasicrystals and Strongly Correlated Electron Systems**

Special session in memory of Prof. An-Pang Tsai at Sakura Hall

## **Memories of Prof. An-Pang Tsai in Institute for Materials Research (1985- 1995) and acknowledgments to him**

**Tsuyoshi Masumoto**  
Emeritus professor,  
Institute for Materials Research,  
Tohoku University

**Akio NIIKURA, Ph.D 新倉昭男**  
Graduated from Masumoto laboratory,  
Institute for Materials Research (IMR),  
Tohoku University.

General Manager  
Design Department  
Automotive Parts Business Division  
UACJ Corporation

# Rough history of Prof. An-Pang Tsai

Year	Event
1958	Born in Taiwan.
1985	Graduated from Akita University
1985	Graduate School of Engineering, Tohoku University. Masumoto laboratory in Institute for Materials Research.
1990	Graduated from Graduate School of Engineering, Tohoku University
1990	Assistant Professor, Masumoto laboratory, Institute for Materials Research. Tohoku university.
1993	Associate Professor, Inoue laboratory, Institute for Materials Research
1996	Chief research officer, National Institute for Materials Science, Tsukuba, Japan
2001	Director, National Institute for Materials Science, Tsukuba, Japan
2004	Professor, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

*Niikura was the graduate student from 1990 to 1995 at Masumoto lab. in IMR.*

# The first studies of quasicrystals in Japan

by Emeritus professor Masumoto

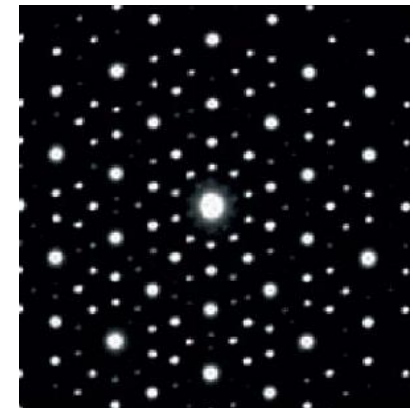
“Icosahedral Quasicrystals of a Melt-Quenched Al-Mn Alloy Observed by High-Resolution Electron-Microscopy”

K.Hiraga, M.Hirabayashi, A.Inoue and T.Masumoto., Sci.Rep. A32(1985), 511~314.

The first studies on quasicrystals in Japan were carried out in the Institute for Materials Research, Tohoku University, as a joint project of Masumoto laboratory and Hirabayashi laboratory. The first paper was due to Prof. Masumoto and Assoc. Prof. Hiraga on the structure analysis of the Al-Mn alloy using electron microscopy.

Dr. Hiraga was at first skeptical about the image, saying that the diffraction pattern looked similar to a multiply twinned sample. But analyzing the sample reproduced by Dr. Inoue, Dr. Hiraga concluded that the diffraction pattern is not from a multiply twinned sample. He started a systematic investigation on samples with different compositions, and the first paper was published in the spring of 1985.

However, the discovery of high-temperature oxide superconductivity was shaking the world (1986). And interests in the lab was largely shifted towards oxide superconductors. There was at least one student who wanted to study ‘quasicrystals’. It was An-Pang Tsai, who later did tremendous discoveries.



Shechtman

Al-18at%Mn

# Masumoto laboratory

## Institute for Materials Research(1987)

Professor Tsuyoshi Masumoto



Associate Professor Akihisa Inoue

Assistant Professor Kiyoshi Aoki  
Kunio Matsuzaki



Graduate student etc.

D3

D2

D1 An-Pang Tsai

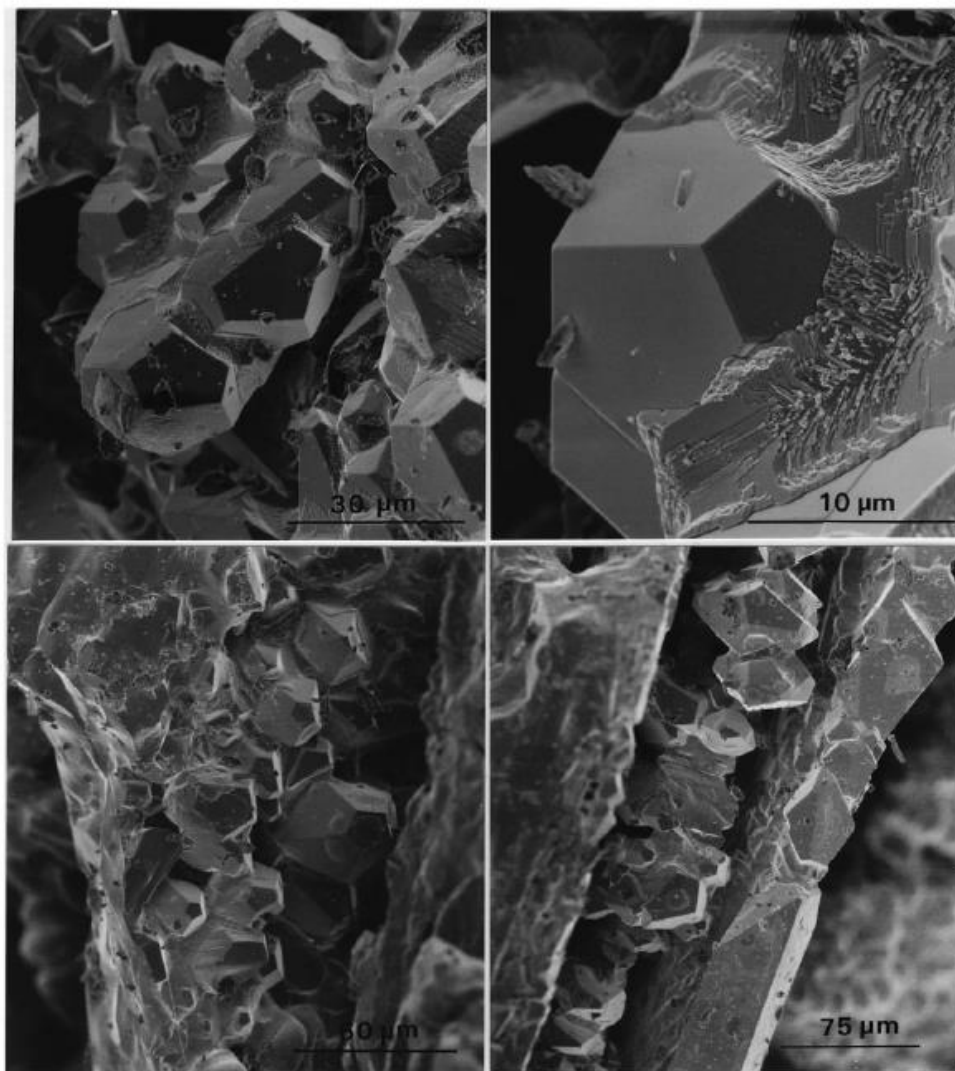
M2 Okumura

M1



# A stable quasicrystal in Al-Cu-Fe system", *Jpn. J. Appl. Physics* **26**, L1505-L1507.(1987)

A.P.Tsai,  
A.Inoue,  
T.Masumoto



*Chem. Soc. Rev.*, 2013,  
**42**, 5352

**Fig. 3** SEM images of the Al<sub>65</sub>Cu<sub>20</sub>Fe<sub>15</sub> alloy prepared by arc melting.

# Scientific Background on the Nobel Prize in Chemistry 2011

## The Nobel Prize in Chemistry 2011



© The Nobel Foundation. Photo: U. Montan

Dan Shechtman

Prize share: 1/1



Scientific Background on the Nobel Prize in Chemistry 2011

## THE DISCOVERY OF QUASICRYSTALS

The Nobel Prize in Chemistry 2011 was awarded to Dan Shechtman "for the discovery of quasicrystals."

※Scientific Background on the Nobel Prize in Chemistry 2011 The Discovery of Quasicrystal (PDF):  
<https://www.nobelprize.org/uploads/2018/06/advanced-chemistryprize2011.pdf>





refer to their respective centering symbols in 6-dimensional superspace. However, while quasicrystals allow non-crystallographic symmetry, they are not defined by it, and quasicrystals with rotational symmetries allowed in normal 3-dimensional space have been found.

A very important factor for the successful determination of quasicrystal structure has been the discovery of stable quasicrystals. Stable quasicrystals may be grown to considerable size and exhibit the typical features of well-ordered crystalline phases. These high-quality samples were necessary for the detailed structural studies that have led to an understanding of quasicrystal structure. The first stable icosahedral quasicrystals were synthesized as early as 1987 in the ternary system Fe-Cu-Al<sup>15</sup>, and stable axial quasicrystals followed the year after<sup>16</sup>. A breakthrough came with the discovery of a binary stable icosahedral quasicrystal in 2000, using Ca-Cd and Yb-Cd<sup>17</sup>. The binary system, which has less disorder, was crucial for providing the high-quality samples subsequently used for the detailed structural elucidation of icosahedral quasicrystals.

<sup>15</sup> A.P. Tsai, A. Inoue, T. Masumoto (1987) "A stable quasicrystal in Al-Cu-Fe system", *Jpn. J. Appl. Physics* **26**, L1505-L1507.

<sup>16</sup> L.X. He, Z. Zhang, Y.K. Wu, K.H. Kuo (1988) "Stable decagonal quasicrystals with different periodicities along the tenfold axis in Al<sub>65</sub>Cu<sub>20</sub>Co<sub>15</sub>", *Inst. Phys. Conf. Ser.* 93 (2), Chapter 13, Conf. EUREM, pp 501–502.

<sup>17</sup> A.P. Tsai, J.O. Guo, E. Abe, H. Takakura, T.J. Sato (2000) "A stable binary quasicrystal" *Nature* **408**, pp 537-538.

<sup>18</sup> U. Dehlinger (1927) "Über die Verbreiterung der Debyelinien bei kaltbearbeiteten Metallen", *Zeitschrift für Kristallographie* **65**, pp 615–631.

<sup>19</sup> P.M. de Wolff (1974) "The pseudo-symmetry of Modulated crystals", *Acta Crystallographica A* **30**, pp 777-785.

<sup>20</sup> A. Janner, T. Janssen (1977) "Symmetry of periodically distorted crystals", *Physical Review B* **15**(2), pp 643–658.

# The first grade doctoral paper was cited in the Nobel Prize award 2011

**Interview of Newspaper to Prof. An-Pang Tsai**

5<sup>th</sup> March 2012

— Why did you decide to start studying quasicrystals?

Research of quasicrystals began in the first year of doctoral course in 1987. When I was a graduate student in Masumoto Lab., I thought that quasicrystals was interesting. So I asked Prof. Masumoto to start new research project quasicrystals. At that time, high temperature oxide superconductor was much more popular, many researchers started to research oxide superconductor. I don't like to be in competition, conversely, I would go forward alone slowly.

— How did you actually advance your research?

At first I investigated how to produce samples by various previous papers. And while I was trying variously, I was able to find a good sample(Al-Cu-Fe) at the relatively early stage of the doctoral course.

At that time there was no culture to submit a paper to "nature", so I submitted it to the "Applied Physics Society of Japan". The paper I wrote at that time, which is probably my first paper in my lifetime, was quoted in the 2011 Nobel Prize for Chemistry Awards.

My first-year doctoral course job was that I found a good sample in the world, which made it clear that it was properties of quasicrystals.



# The first grade doctoral paper was cited in the Nobel Prize award 2011

**Interview of Newspaper to Prof. An-Pang Tsai**

5<sup>th</sup> March 2012

- How can you discover almost 90% quasicrystals?

I am always considering "Why can we produce quasicrystals".

"why?" "I wonder if something will happen." "I will prove my idea by the experiment." I proceed checking various things, and I try again based on principles. Then I understand the draft reason for "Why can we produce quasicrystals? "

-There is always a question asking "Why can we make quasicrystals?" at the root of the process, rather than the purpose of making quasicrystals itself.

While repeating that " if this principle would be true, I also would be possible another idea. " Of course, I think more intelligent researcher consider more and calculate more. The experimenter myself consider "Why is this?" If this concept is correct, next step should also be possible.

# Rough history of Prof. An-Pang Tsai

Year	Event
1858	Born in Taiwan.
1985	Graduated from Akita University
1985	Graduate School of Engineering, Tohoku University. Masumoto laboratory in Institute for Materials Research.
1990	Graduated from Graduate School of Engineering, Tohoku University
1990	Assistant Professor, Masumoto laboratory, Institute for Materials Research. Tohoku university.
1993	Associate Professor, Inoue laboratory, Institute for Materials Research
1996	Chief research officer, National Institute for Materials Science, Tsukuba, Japan
2001	Director, National Institute for Materials Science, Tsukuba, Japan
2004	Professor, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

*I was a graduate school student from 1990 to 1995 at Masumoto lab. in IMR.*

# Masumoto laboratory

## Institute for Materials Research(1993)

Professor Tsuyoshi Masumoto

Associate Professor Kiyoshi Aoki

Assistant Professor **An-Pang Tsai**

Tomoyasu Aihara

Graduate student:

D3 Kawamura, Okumura, Zhang,

D2 Yokoyama,

D1 **Niikura**, Mori, Paku

M2 Kawase, Memezawa, Nakazato

M1 Ishikawa, Aoyagi, Tsurui

Research student from company; 8



**Table 2.** Type of structure for stable.

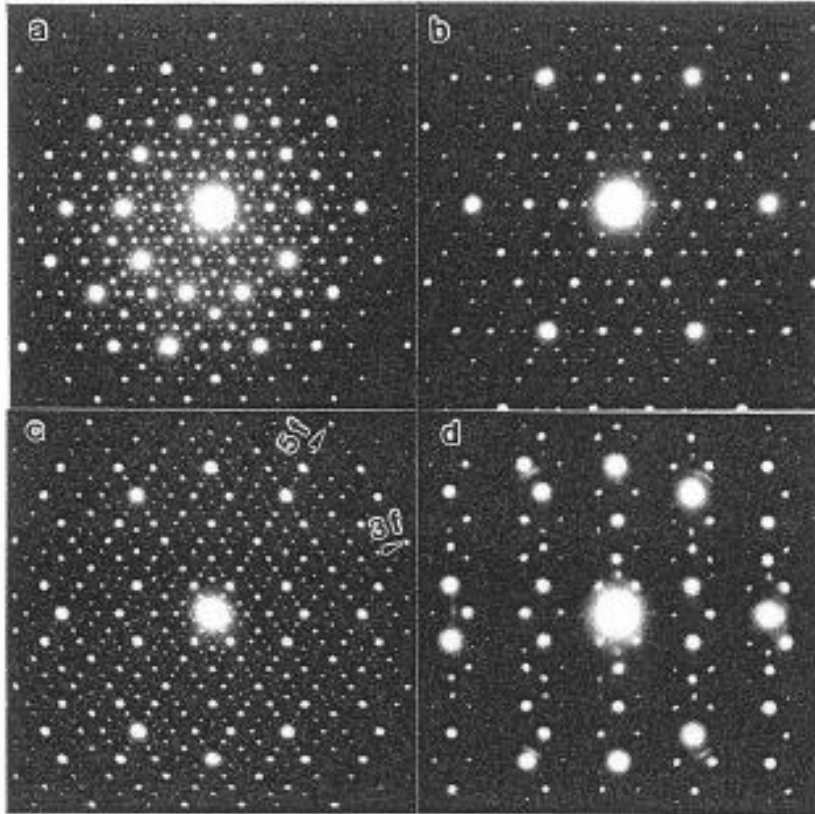
P-type		F-type
Al–Mn–Si		Al <sub>63</sub> Cu <sub>25</sub> TM <sub>12</sub> (TM:Fe Ru Os) Al <sub>70</sub> Pd <sub>20</sub> TM <sub>10</sub> (TM:Mn Tc Re)
Zn–Mg–Al	Al <sub>5</sub> Li <sub>3</sub> Cu	Zn <sub>60</sub> Mg <sub>30</sub> RE <sub>10</sub> (RE:Y Dy Ho Gd Er Tb)
	Zn <sub>70</sub> Mg <sub>20</sub> RE <sub>10</sub> (RE:Er Ho)	<u>Zn<sub>74</sub>Mg<sub>19</sub>TM<sub>7</sub>(TM:Zr Hf)</u>
Cd–Yb	Cd <sub>5.7</sub> M(M:Yb Ca)	
	Cd <sub>65</sub> Mg <sub>20</sub> M <sub>15</sub> (M:Yb Ca Y Ho Gd Er Tb)	
	Zn <sub>80</sub> Mg <sub>5</sub> Sc <sub>15</sub>	
	In <sub>42</sub> Ag <sub>42</sub> M <sub>16</sub> (M:Yb Ca)	
	Zn <sub>74</sub> Ag <sub>10</sub> Sc <sub>16</sub> , Zn <sub>75</sub> Pd <sub>9</sub> Sc <sub>16</sub>	
	Zn <sub>77</sub> Fe <sub>7</sub> Sc <sub>16</sub> , Zn <sub>78</sub> Co <sub>6</sub> Sc <sub>16</sub> Zn <sub>75</sub> Ni <sub>10</sub> Sc <sub>15</sub>	

The first evidence of an IQC in this system was observed at grain boundaries in commercial Mg alloys by Tang et al. In a follow up to this work, we identified a group of stable IQCs in Zn–Mg–RE (RE: Y, Gd, Tb, Dy, Ho, Er) in 1994.

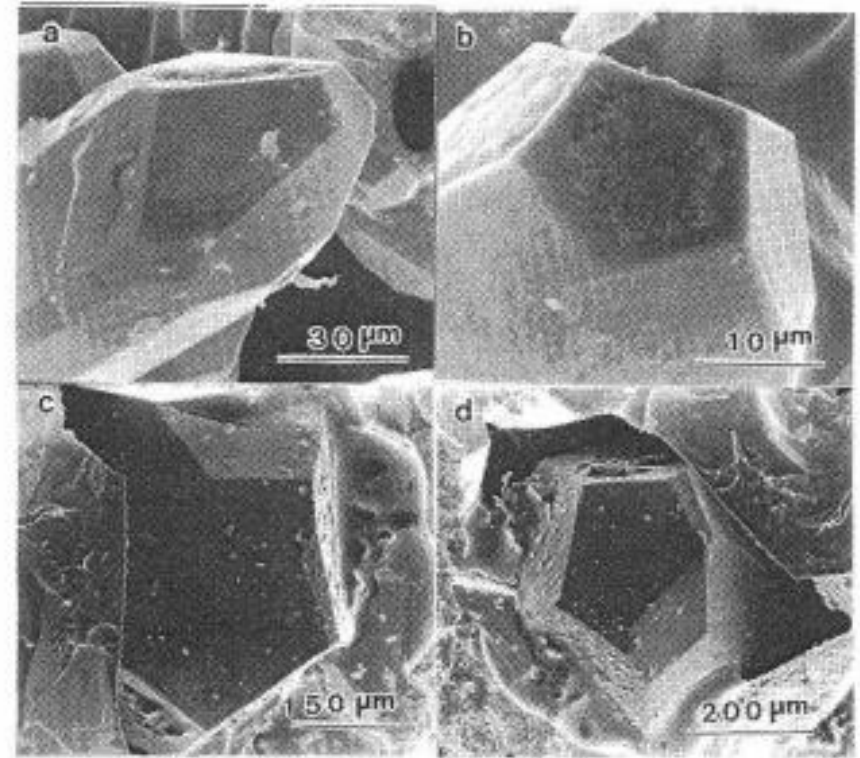
# Stable Zn-Mg-Rare-Earth Face-Centered Icosahedral Alloys With Pentagonal Dodecahedral Solidification Morphology

A.Niikura, A.P.Tsai, A.Inoue, T.Masumoto

Philosophical Magazine Letters 69(6)1994:351-355



a,b,c  $\text{Zn}_{50}\text{Mg}_{42}\text{Y}_8$   
d  $\text{Al}_6\text{Li}_3\text{Cu}_1$



873K, 1h → 623K, 24h  
1K/min

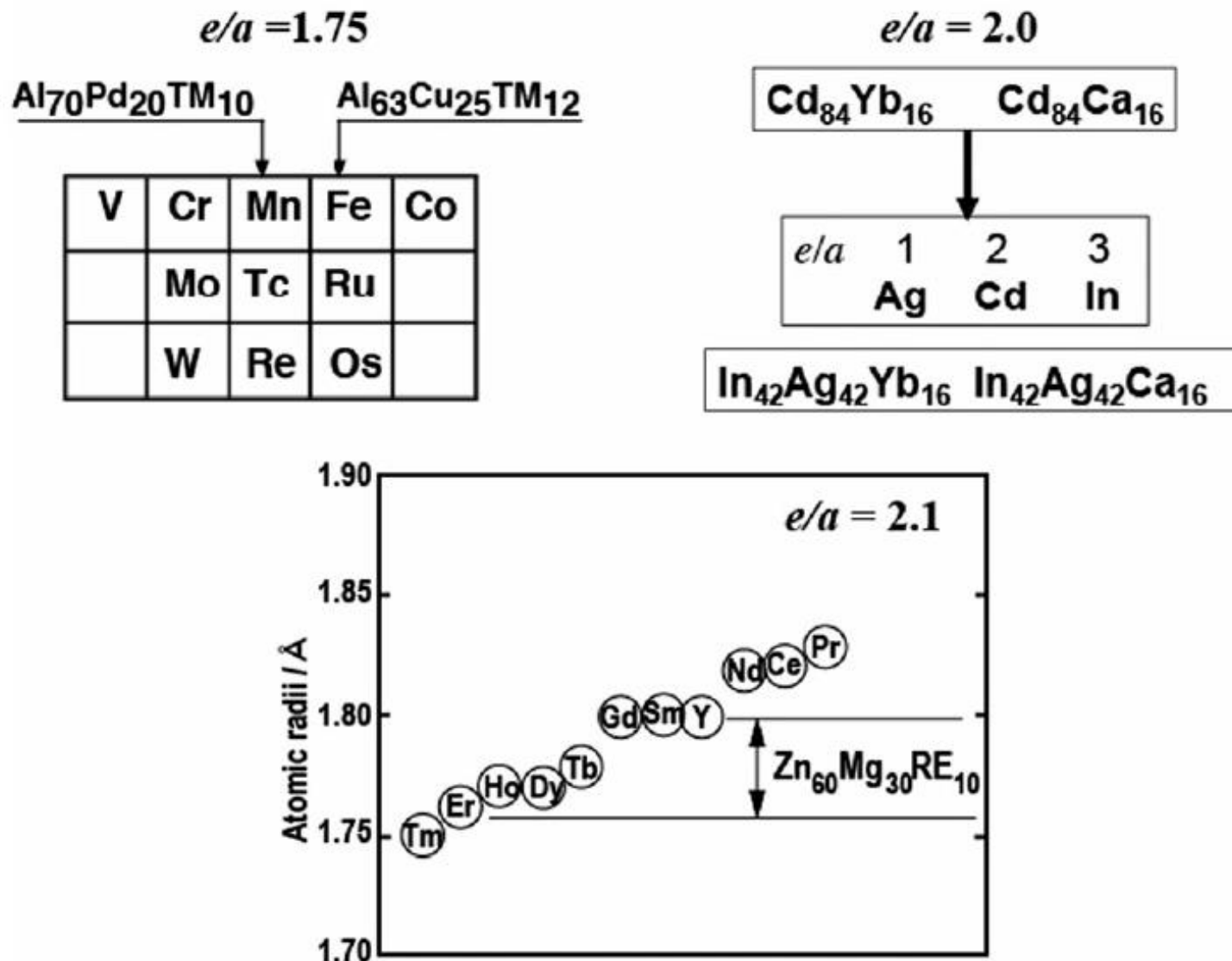
# Highly ordered structure of icosahedral quasicrystals in Zn-Mg-RE (RE =rare earth metals) systems

TSAI A P, NIIKURA A, INOUE A, MASUMOTO T, NISHIDA Y, TSUDA K, TANAKA M  
 Philosophical Magazine Letters 70(3)1994:169-175

		Stable phase	Metastable phase
FK-type	P-type	$\text{Al}_3\text{Li}_3\text{Cu}$ $\text{Mg}_{45}\text{Pd}_{14}\text{Al}_{41}$ $\text{Ga}_{10}\text{Mg}_{18}\text{Zn}_{21}$	$\text{Mg}_{32}(\text{Al,Zn})_{49}$ , $\text{Al}_8\text{Li}_3\text{Au}$ $\text{Al}_{50}\text{Mg}_{35}\text{Ag}_{15}$ , $\text{Al}_5\text{Mg}_4\text{Cu}$
	F-type	<b><math>\text{Zn}_{50}\text{Mg}_{42}\text{RE}_8</math> (RE=Y,Gd, Tb, Dy, Ho, Er)</b>	
	MI-type		$\text{Al-Mn}$ , $\text{Al-Cr}$ , $\text{Al-V}$ $\text{Al}_{72}\text{Mn}_{20}\text{Si}_8$ , $\text{Al}_{72}\text{V}_{20}\text{Si}_8$ , $\text{Al}_{75}\text{Cu}_{15}\text{V}_{10}$ , $\text{Pd}_{60}\text{U}_{20}\text{Si}_{20}$ $\text{Al}_{40}\text{Mn}_{25}\text{Cu}_{10}\text{Ge}_{25}$ $\text{Ga-Pd-(Cr,Mn,Fe)}$
$aR/a = 1.75$ $e/a = 2.2$	P-type		
	F-type	$\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ $\text{Al}_{65}\text{Cu}_{20}\text{Os}_{15}$ $\text{Al}_{65}\text{Cu}_{20}\text{Ru}_{15}$ , $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ , $\text{Al}_{70}\text{Pd}_{20}\text{Re}_{10}$	$\text{Al-Pd-TM}$ $\text{Al-Cu-TM}$
$aR/a = 1.65$ $e/a = 1.75$	Others		$\text{Ti}_{36}\text{Ni}_{28}\text{Si}_{16}$ , $\text{V}_{41}\text{Ni}_{36}\text{Si}_{23}$ $\text{Ti}_{36}\text{Ni}_{13}\text{Fe}_{15}\text{Si}_{16}$



The  $e/a$  criterion for several stable IQCs of various alloy systems.



**Fig. 12** Formation of stable IQCs dominated by  $e/a$  in three families of IQCs.

*Chem. Soc. Rev.*, 2013, **42**, 5352

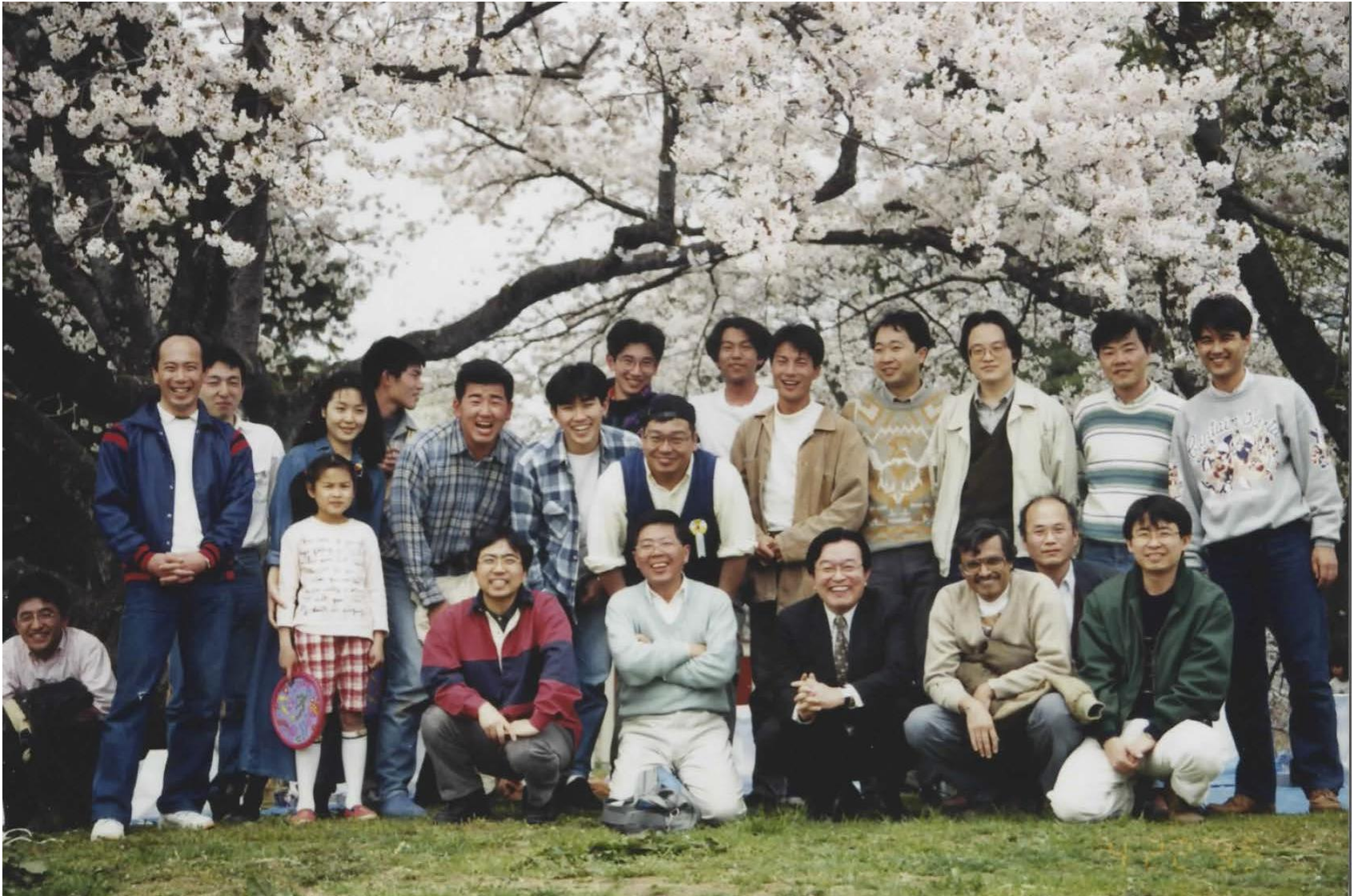
# 1990 Activities in Masumoto laboratory

## Assistant Professor





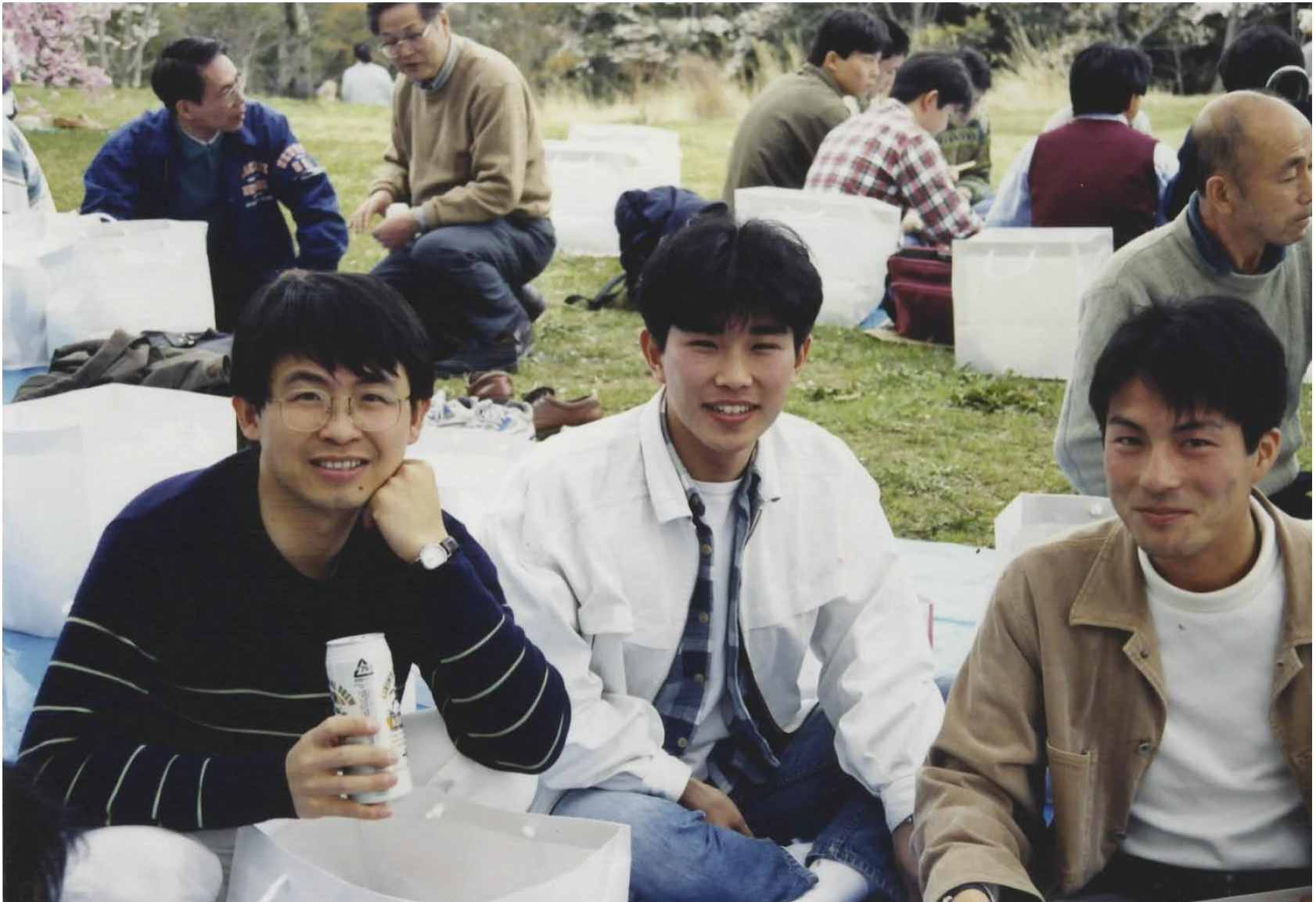
# 1992 Activities in Masumoto laboratory Assistant Professor





# 1993 Activities in Inoue laboratory

## Associate Professor



# 2007 Masumoto material forum





# 2007 Masumoto material forum

増本金属材料フォーラム

日 時： 平成19年4月21・22日

場 所： 緑水亭（宮城県仙台市太白区秋保町湯元上原 27）

プログラム：

●シンポジウム（13：30－17：45）

13：30－13：40 開会の挨拶（青木 清）

司会 青木 清

13：40－14：25 増本 健 先生

「金属－セラミックス系ナノ複合薄膜の開発と応用」





# 2012 Nobel Prize Lecture at the Japan Institute of Metals by Prof. Dan Sechtman



## Nobel Prize for Chemistry "Discoverer of Quasicrystals"



Spring 2012 The Japan Institute of Metals and Materials

# May 2015 Celebration of Purple Ribbon Medal

蔡先生紫綬褒章受章祝賀会  
日時 平成27年3月20日(金)  
会場 學士會館 202会場



I have learned the basics as a researcher from Prof. An-Pang Tsai. I am deeply grateful for his education, training and support in my life. I would like to offer my condolences for the loss of Prof. An-Pang Tsai. In deepest sympathy.