# High temperature vacancy studies of icosahedral $Zn_{65}Mg_{25}Er_{10}$ quasicrystal



2004 J. Phys.: Condens. Matter 16 1531

(http://iopscience.iop.org/0953-8984/16/9/002)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 1531–1537 PII: S0953-8984(04)73094-5

# High temperature vacancy studies of icosahedral $Zn_{65}Mg_{25}Er_{10}$ quasicrystal

**F Ye[1,2], W Sprengel[1], X Y Zhang[1,3], E Uhrig[4], W Assmus[4] and H-E Schaefer[1]**

[1] Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57/VI, D-70550 Stuttgart, Germany
[2] Max-Planck-Institut für Metallforschung, Heisenbergstraße 1, D-70569 Stuttgart, Germany
[3] College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, People's Republic of China
[4] J W Goethe-Universität, Physikalisches Institut, D-60054 Frankfurt/Main, Germany

E-mail: ye@itap.physik.uni-stuttgart.de

Received 5 December 2003
Published 20 February 2004
Online at stacks.iop.org/JPhysCM/16/1531 (DOI: 10.1088/0953-8984/16/9/002)

**Abstract**

Formation of thermal vacancies in icosahedral $Zn_{65}Mg_{25}Er_{10}$ quasicrystals has been specifically studied from room temperature to about 720 K by positron annihilation spectroscopy employing two-detector coincident Doppler broadening techniques. Significant vacancy formation was observed for temperatures higher than $0.6T_m$. An apparent vacancy formation enthalpy of 1.2 eV was determined. The results are discussed in comparison with high temperature vacancy processes in quasicrystals as well as in other complex solids.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Quasicrystals are well ordered complex solids with an aperiodic lattice structure. The first quasicrystal discovered in 1984 by Shechtman *et al* [1] belongs to a group of mostly Al based icosahedral alloys such as AlLiCu, AlPdMn, AlCuFe and AlMgZn. In 1993 a Zn based icosahedral quasicrystal was found in the Zn–Mg–RE (RE = rare earth) alloy system [2]. The structures and properties of these ZnMgRE quasicrystals have been extensively investigated [3–6], because ZnMgRE quasicrystals with a 10–11 at.% rare earth metal content belong to the group of most perfect thermodynamically stable icosahedral quasicrystals. Their structures are considered to be of the Frank–Kasper type [7], which is characterized by an electron per atom ratio of $e/a = 2.1$.

Similar to those in periodic solids, lattice vacancies in quasicrystals play a decisive role in atomic processes which determine atomic diffusion, plastic deformation or structural phase

  

transformations. For the study of vacancies in quasicrystals, positron annihilation techniques have been proved to provide specific information on atomic vacancies in quasicrystals at both ambient [8] and high temperatures [9]. The results confirmed a dense distribution of structural vacancies (of the order of $10^{-3}$) [8–11], which could not be removed even by long term annealing [12]. Thermally formed vacancies were observed in AlPdMn quasicrystal by two-detector coincident Doppler broadening spectroscopy of the electron–positron annihilation photons [9, 13].

The aim of this work is to study the formation of thermal vacancies in the icosahedral ZnMgEr quasicrystal by *in situ* high temperature coincident Doppler broadening measurements of the positron–electron annihilation radiation.

## 2. Experiment

Single-grain $Zn_{65}Mg_{25}Er_{10}$ quasicrystal was grown from the melt by the liquid encapsulated top seeded solution growth method [14]. From this single-grain quasicrystal, a cylindrical barrel, with an outer diameter of 5 mm, inner diameter of 2 mm and height of 6 mm, was prepared for the high temperature positron annihilation experiments. A $^{58}CoCl_3$ positron source in solution was deposited into the hole of the barrel, reduced and diffused during high temperature annealing in hydrogen. With a subsequent tight covering by a cap of the same material, the ZnMgEr specimen was sealed in the quartz tube ($p \sim 10^{-3}$ Pa).

By means of two high resolution Ge detectors, coincident Doppler broadening measurements of the positron–electron annihilation $\gamma$ spectra up to high momenta of the chemically characteristic core electrons were carried out at varied temperature by measuring the two annihilation photons with the energies $E_1$ and $E_2$ in coincidence. The high peak-to-background ratio ($>5\times10^5$) was achieved by diagonal cuts of the $E_1-E_2$ Doppler spectra along the $E_1 + E_2 = 1022 \pm 1.5$ keV energy line. Each of these spectra contains more than $2 \times 10^7$ coincidence counts, achieving good statistics in the core electron region above $\Delta E = 5$ keV, which corresponds to $P_L \geqslant 20 \times 10^{-3} m_0 c$ for the core electron momenta. To emphasize the high momentum tails, the Doppler broadening spectra measured for ZnMgEr, Zn and Mg were normalized to the smoothed Zn spectrum so that the Zn spectrum is represented by a straight horizontal line.

## 3. Results and discussion

Three runs of positron annihilation measurements: heating, heating after quenching and slow cooling were carried out on a $Zn_{65}Mg_{25}Er_{10}$ quasicrystal sample in the temperature range from room temperature to 720 K.

The temperature variation of the $S$ parameter during heating and cooling the specimen is plotted in figure 1. The $S$ parameter, which provides a measure of the annihilation fraction with valence electrons, was determined by the ratio of the central area over $[-2.5, +2.5]$ $(10^{-3} m_0 c)$ to the total area of the Doppler broadening spectrum after subtracting the background. Here, $m_0$ denotes the electron mass and $c$ the velocity of light. The $S$ parameter increases with temperature from about 0.49 at 293 K to 0.51 at 700 K, indicating an enhancement of the open volume in the ZnMgEr quasicrystal at high temperature. It should be noted that the $S$ parameter of ZnMgEr quasicrystal is quite large in comparison with previous results [15] for ZnMgHo ($\sim$0.22) and AlPdMn ($\sim$0.23). This is due to the different calculation methods. Table 1 lists the $S$ and $W$ parameters of ZnMgEr, ZnMgHo and AlPdMn quasicrystals calculated by the new software. It can be seen that the $S$ parameters are very close for the three quasicrystals.

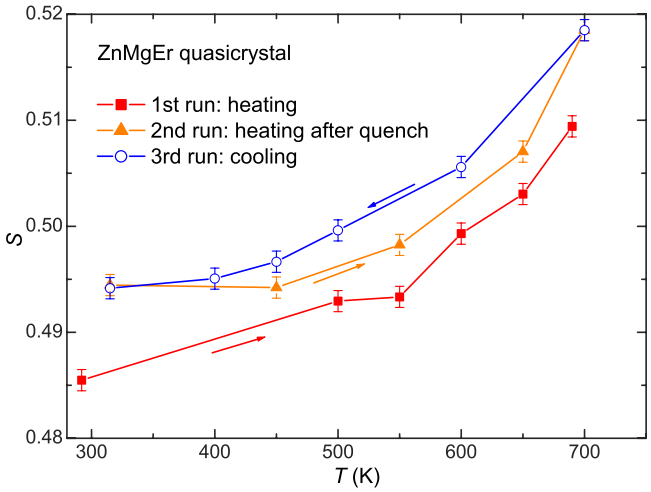


**Figure 1.** The temperature variation of the $S$ parameter of icosahedral $Zn_{65}Mg_{25}Er_{10}$ quasicrystals. The $S$ parameter has been determined for the range of $P_L < 2.5 \times 10^{-3} m_0 c$. The figure shows the total temperature history of the specimen: ■, initial heating run; △, second heating run after quenching to 293 K; ○, third run, upon slow cooling. Arrows indicate the measuring sequence of the data points.

**Table 1.** $W$ and $S$ parameters derived from the Doppler broadening spectra of positron annihilation, as well as the positron lifetime $\tau_1$, in quasicrystals at ambient and high temperatures.

| Compound | Temperature (K) | $\tau_1$ (ps) | $S$ | $W$ ($10^{-3}$) |
|---|---|---|---|---|
| $Zn_{64}Mg_{26}Ho_{10}$ | 293 | 203 | 0.49 | 4.48 |
| $Zn_{65}Mg_{25}Er_{10}$ | 293 | 196 | 0.49 | 4.58 |
| | 720 | | 0.52 | 4.02 |
| $Al_{70}Pd_{21}Mn_9$ | 293 | 206 | 0.47 | 2.20 |
| | $\sim T_m$ | | 0.48 | 2.02 |

The $S$ parameters measured in the second heating run are slightly higher than the values obtained in the first heating run (figure 1). This might be due to quenched-in residual thermal vacancies formed during the first heating run.

For an analysis of the core electron contribution in the Doppler broadening spectra, a $W$ parameter covering the range (18–25) $\times 10^{-3} m_0 c$ with normalization to the total area of the spectrum was employed. The high momentum Doppler broadening $W$ parameters (figure 2) present an S-shaped curve at high temperatures superimposed on a linear slope at low temperatures. The significant decrease of the $W$ parameter at about 560 K indicates the formation of thermal vacancies in the ZnMgEr quasicrystal. The linear decrease of the $W$ parameter at low temperatures also shows the existence of structural vacancies. This can be further proved by a single-positron lifetime of 196 ps, which was detected in ZnMgEr quasicrystal at room temperature with a $^{22}$Na source. The ZnMgEr quasicrystal exhibits a long positron lifetime, as for other quasicrystals (table 1), which means that the positrons were annihilated at the structural vacancies as discussed in previous work [9].

The ratio curves of the coincident Doppler broadening spectra of ZnMgEr at different temperatures are shown in figure 3. They are located between the spectra of Zn, Mg and Ho. As Er has a similar electron configuration to Ho, we conclude that both the structural and thermal vacancies are surrounded by Mg, Zn and Er atoms. With increasing temperature, the

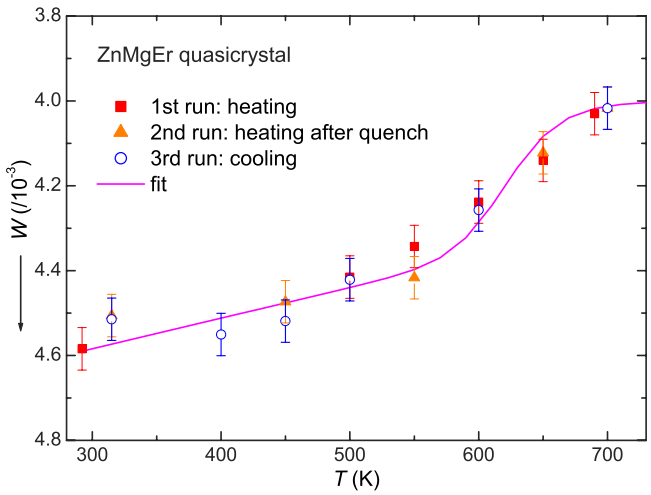


**Figure 2.** The reversible temperature variation of the $W$ parameter for icosahedral $Zn_{65}Mg_{25}Er_{10}$ quasicrystal. The $W$ parameter has been determined for the range of $18 < P_L < 25 \times 10^{-3} m_0 c$. The solid curve is a fit of the data according to equations (1) and (2).

ratio spectrum of ZnMgEr is significantly shifted apart from that of pure Zn and towards those of Ho and Mg in the core electron momentum range of (10–20) $\times 10^{-3} m_0 c$. It was reported that electron irradiation induced vacancies shift the spectra of ZnMgHo quasicrystal towards that of pure Zn [15]. The present result implies the different possibilities for each atomic site to form structural vacancies and thermal vacancies.

The results of the Doppler broadening measurements reveal that the positron annihilation behaviours for the ZnMgEr and ZnMgHo quasicrystals are very alike, implying similar atomic structures and properties. Very similar $W$ parameters were obtained from ZnMgEr and ZnMgHo quasicrystals at 293 K, which are much larger than that of AlPdMn quasicrystal (table 1). From the Doppler broadening spectra (figure 3), one can also see that the spectra are almost identical at room temperature for ZnMgEr and ZnMgHo quasicrystals.

In order to estimate the vacancy formation enthalpy $H_V^F$ in ZnMgEr quasicrystal, the S-shaped high temperature change of the $W$ parameter can be modelled by

$$W(T) = \frac{W_1 + \frac{\sigma_2}{\sigma_1 C_1} W_2 C_2}{1 + \frac{\sigma_2}{\sigma_1 C_1} C_2} \tag{1}$$

with the temperature-dependent concentration

$$C_2 = \exp(S_V^F / k_B) \exp(-H_V^F / k_B T) \tag{2}$$

of thermal vacancies. Here, $W_1 = W_{1,0}(1 - \beta_2 T)$ is the temperature-dependent characteristic $W$ parameter of the structural vacancies, $W_2$ the $W$ parameter characteristic for thermal vacancies, $\sigma_2/\sigma_1 \approx 1$ the ratio of the specific positron trapping rates of thermal and structural vacancies, $C_1 \approx 10^{-3}$ the concentration of structural vacancies and $S_V^F$ the vacancy formation entropy. From the fit of equations (1) and (2) to the data in figure 2 we obtain

$$H_V^F = 1.2 \pm 0.1 \text{ eV} \tag{3}$$

$$\frac{\sigma_2}{\sigma_1 C_1} \exp(S_V^F / k_B) = (3.0 \pm 1) \times 10^9 \text{ s}^{-1}, \tag{4}$$

$$W_{1,0} = (4.80 \pm 0.02) \times 10^{-3}, \qquad W_2 = (4 \pm 0.02) \times 10^{-3} \tag{5}$$

and the temperature coefficient $\beta_2 = (1.5 \pm 0.1) \times 10^{-4}$ K$^{-1}$.

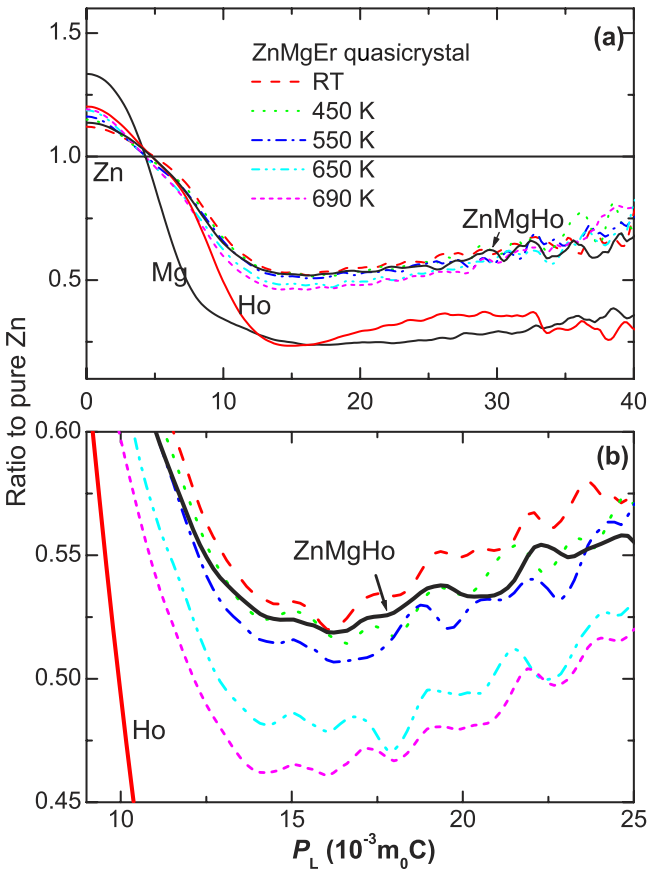


**Figure 3.** The Doppler broadening ratio spectra of $Zn_{65}Mg_{25}Er_{10}$ quasicrystal from room temperature to 690 K together with the spectra of Zn, Mg, Ho pure elements and ZnMgHo quasicrystal. Each spectrum is normalized to the Doppler broadening spectrum of pure Zn at room temperature.

The S-shaped curves of the $W$ parameters, depending on temperature, for $Al_{70}Pd_{21}Mn_9$ and $Zn_{65}Mg_{25}Er_{10}$ are shown in figure 4 for comparison. The curves are calculated from equation (1) with the parameters from [13] and the present work, respectively. The $W$ parameters were plotted as a function of reduced temperature $T/T_m$ with $T_m$ the melting temperature. $T_m$ is about 934 K for $Zn_{65}Mg_{25}Er_{10}$ and 1159 K for $Al_{70}Pd_{21}Mn_9$ [16]. The differences between the $W$ parameter characteristics of the two quasicrystals are significant. The thermal formation of vacancies in icosahedral ZnMgEr occurs over a wider temperature range than in icosahedral AlPdMn. The formation of thermal vacancies begins at $0.72T_m$ in AlPdMn and at $0.60T_m$ in ZnMgEr. The decrease of the $W$ parameter from ambient to $T_m$ due to the structural vacancies could be estimated as 0.34 and $0.02 \times 10^{-3}$ for ZnMgEr and AlPdMn, respectively, while the contributions of the thermal vacancies are 0.26 and $0.13 \times 10^{-3}$, respectively. These factors suggest that structural vacancies play a more important role in the high temperature process in ZnMgEr.

The apparent vacancy formation enthalpy $H_V^F = 1.2$ eV for ZnMgEr is much smaller than the value derived from AlPdMn (∼2.3 eV) when normalized to the melting temperature, indicating that thermal vacancy formation in ZnMgEr is much easier than in AlPdMn [13].

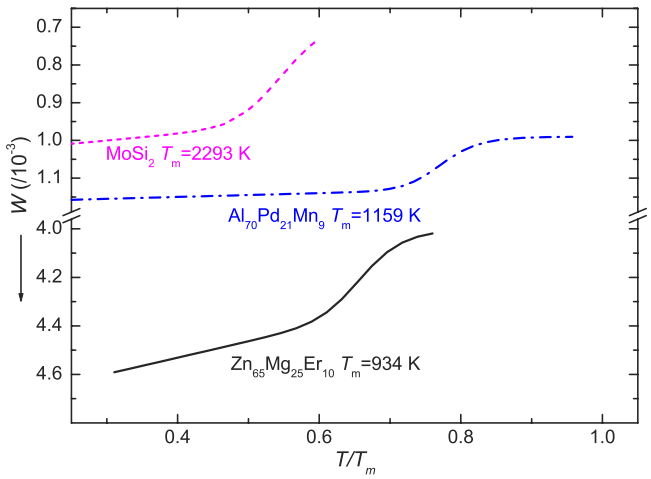


**Figure 4.** The calculated $W$ parameters as functions of reduced temperature $T/T_m$ for $Zn_{65}Mg_{25}Er_{10}$ and $Al_{70}Pd_{21}Mn_9$ quasicrystals, as well as the intermetallic compound $MoSi_2$.

**Table 2.** Data on thermal vacancy formation in various complex solids and pure metals. $T_m$: melting temperature; $T_s$: onset temperature of significant thermal vacancy formation; $H_V^F$: vacancy formation enthalpy. Among these materials, the structural vacancies exist only in the quasicrystals ZnMgEr and AlPdMn.

| Compound | $T_m$ (K) | $T_s/T_m$ | $H_V^F$ (eV) | $H_V^F/k_BT_m$ | References |
|---|---|---|---|---|---|
| $MoSi_2$ | 2293 | 0.45 | 1.6 | 6 | [18] |
| $Zn_{65}Mg_{25}Er_{10}$ | 934 | 0.60 | 1.2 | 15 | This work |
| $Al_{70}Pd_{21}Mn_9$ | 1159 | 0.72 | 2.3 | 17 | [13] |
| Cu (fcc) | 1358 | 0.58 | 1.1–1.3 | 7–8 | [19] |
| Mo (bcc) | 2896 | 0.62 | 3.6 | 11 | [19] |
| Al (fcc) | 933 | 0.47 | 0.7 | 6 | [19] |

The only diffusion data on ZnMgRE quasicrystal are from the self-diffusion of $^{65}Zn$ in i-ZnMgHo, which provided for the first time diffusion data for the main component of a quasicrystal [17]. An activation energy of 1.56 eV was obtained and the conclusion that the Zn self-diffusion in ZnMgHo is vacancy mediated was drawn. Considering the higher melting temperature of ZnMgEr, the activation energy for Zn self-diffusion in ZnMgEr might be about 1.7 eV. It can be seen that our result agrees well with the diffusion measurements and supports the vacancy mechanism for self-diffusion in quasicrystals. Supposing the diffusion activation energy is the sum of the enthalpies of vacancy formation and migration, the vacancy migration enthalpy could be 0.5 eV. This high value does not agree well with the phenomenon observed in positron lifetime spectra of ZnMgHo [15] which implies a high mobility of the vacancy.

Finally we compare the thermal vacancy formation between quasicrystals and intermetallic compounds. Figure 4 also includes a plot of the temperature dependence of the $W$ parameter for $MoSi_2$. Because there are no structural vacancies in $MoSi_2$, the $W$ parameters were fitted by a different model [18]. It can be seen that the thermal vacancy formation begins at about $0.45T_m$ for $MoSi_2$, which is quite a lot lower than the values for quasicrystals. Table 2 compares the formation temperature and the formation enthalpy for the thermal vacancy in various complex solids and pure metals. The $T_s/T_m$ values for quasicrystals are fairly high, which indicates the specific structure and properties of quasicrystals.

## 4. Conclusion

By means of coincident Doppler broadening measurements the formation of thermal vacancies in icosahedral ZnMgEr quasicrystal was observed. An apparent vacancy formation enthalpy $H_V^F = 1.2$ eV was derived by fitting the temperature dependence of the $W$ parameter variation in a simple model. The result supports the vacancy mechanism for self-diffusion in quasicrystals.

## Acknowledgments

Financial support of the German Research Foundation (SCHA 428/22), the Max-Planck Society (Munich, Germany) and the Max-Planck Institute for Metal Research (Stuttgart, Germany) is appreciated.

## References

[1] Shechtman D, Blech I, Gratias D and Cahn J W 1984 *Phys. Rev. Lett.* **53** 1951
[2] Luo Z, Zhang S, Tang Y and Zhao D 1993 *Scr. Metall. Mater.* **28** 1513
[3] Tsai A P, Niikura A, Inoue A, Masumoto T, Nishida Y, Tsuda K and Tanaka M 1994 *Phil. Mag. Lett.* **70** 169
[4] Langsdorf A, Ritter F and Assmus W 1997 *Phil. Mag. Lett.* **75** 381
[5] Rouijaa M, Suck J-B, Sterzel R and Petrenko O A 2002 *J. Alloys Compounds* **342** 314
[6] Sterzel R, Gross C, Kounis A, Miehe G, Fuess H, Reutzel S, Holland-Moritz D and Assmus W 2002 *Phil. Mag. Lett.* **82** 443
[7] Niikura A, Tsai A P, Inoue A and Masumoto T 1994 *Phil. Mag. Lett.* **69** 351
[8] Sato K, Takahashi Y, Uchiyama H, Kanazawa I, Tamura R, Kimura K, Komori F, Suzuki R, Ohdaira T and Takeuchi S 1999 *Phys. Rev.* B **59** 6712
[9] Baier F and Schaefer H-E 2002 *Phys. Rev.* B **66** 064208
[10] Würschum R, Grushko B, Urban K and Schaefer H-E 1994 *Phil. Mag.* B **70** 913
[11] Kanazawa I, Hamada E, Saeki T, Sato K, Nakata M, Takeuchi S and Wollgarten M 1997 *Phys. Rev. Lett.* **79** 2269
[12] Baier F, Müller M A, Sprengel W, Grushko B, Sterzel R, Assmus W and Schaefer H-E 2001 *Mater. Sci. Forum* **363–365** 179
[13] Sato K, Baier F, Rempel A A, Sprengel W and Schaefer H-E 2004 at press
[14] Langsdorf A and Assmus W 1999 *Cryst. Res. Technol.* **34** 261
[15] Sato K, Baier F, Sprengel W and Schaefer H-E 2002 *Phys. Rev.* B **66** 092201
[16] Zumkley T and Nakajima H 2000 *Phil. Mag.* A **80** 1065
[17] Mehrer H and Galler R 2002 *J. Alloys Compounds* **342** 296
[18] Zhang X Y, Sprengel W, Blaurock K, Reichle K J, Inui H and Schaefer H-E 2004 at press
[19] Schaefer H-E 1987 *Phys. Status Solidi* a **102** 47