

EXAFS Analysis of Zr-Based Quasicrystals

A. P. Menushenkov^a, O. V. Kashurnikova^a, R. V. Chernikov^a,
K. V. Klementiev^b, G. Kh. Panova^c, and A. A. Shikov^c

^a Moscow Engineering Physics Institute, Kashirskoe sh. 31, Moscow, 115409 Russia
e-mail: menushen@htsc.mephi.ru

^b ALBA CELLS, 08193 Bellaterra, Barcelona, Spain.

^c Russian Research Centre Kurchatov Institute, pl. Akademika Kurchatova 1, Moscow, 123182 Russia

Abstract—The character of transformation of the local structure of zirconium and palladium atoms in Zr₇₀Pd₃₀ binary alloy at a transition from the amorphous state to the quasicrystalline and crystalline states and in Zr₇₀Be₃₀ and Zr₈₀Pt₂₀ binary alloys at a transition from the amorphous to the quasicrystalline state have been investigated by extended X-ray absorption fine-structure (EXAFS) spectroscopy and X-ray diffraction. The parameters of the zirconium, palladium, and platinum local structure are determined, and the general features and differences in the local atomic rearrangement during formation of icosahedral clusters around zirconium atoms in these three compounds are established.

DOI: 10.3103/S1062873808100389

The quasicrystalline state of matter, which is intermediate between the amorphous and crystalline states [1], has a number of unusual properties, such as high microhardness; strength; low wetting; and some peculiar electronic properties, which are related to the existence of a pseudogap in the electronic spectrum. Therefore, quasicrystals can be widely and effectively used as additives modifying the surface properties of metals and alloys, non-stick coatings, antifriction additives, etc. The quasicrystalline state of Zr₇₀Pd₃₀, Zr₇₀Be₃₀, and Zr₈₀Pt₂₀ binary alloys is formed in spite of the empirical rules of glass formation, established for Zr-based alloys; in particular, the multicomponent composition rule [2]. Hence, the specific features of their local atomic structure are of great interest.

In this paper, we report the results of the investigation of the changes in the local structure of Zr-based binary alloys at the phase transitions from the amorphous to the quasicrystalline state and from the crystalline to the quasicrystalline state (for Zr₇₀Pd₃₀).

The Zr₇₀Pd₃₀ alloy was prepared at the Russian Research Centre Kurchatov Institute by the technique described in [3], from electrolytically pure zirconium (99.99%) and pure palladium (99.96%). Polycrystalline Zr₇₀Pd₃₀ samples were grown in an induction furnace in argon. To obtain amorphous samples, starting elements were placed in a boron nitride ampoule, melted in the induction furnace under low argon pressure, and rapidly (at a rate of 10⁶ K/s) quenched from the liquid state onto the outer surface of a rotating copper cylinder. Quasicrystalline samples were prepared by annealing the thus obtained amorphous ribbons with a width of 1.5–2 mm and a thickness of ~30 μm in a helium gas flow through a quartz tube placed in a muffle furnace.

The preparation conditions for the most perfect icosahedral sample was optimized by annealing at several temperatures (740 and 760 K) with subsequent rapid quenching. The structure of the samples and the effect of annealing on their state were analyzed using a DRON-2 diffractometer in CuK_α radiation. The phase analysis was performed on the basis of the X-ray diffraction patterns.

According to the X-ray diffraction data, the crystalline phase has the symmetry group *I4/mmm* with the lattice parameters *a* = 3.306 Å and *c* = 10.894 Å. The X-ray diffraction analysis of the quasicrystalline phase according to Bansel [4] showed the presence of an icosahedral structure with the hypercubic lattice parameter *a* = 7.624 Å. At an annealing temperature of 760 K, the quality of the quasicrystalline phase was higher; however, with a further increase in temperature and annealing time, crystalline phase began to form in the samples. Annealing at 873 K led to complete recovery of the crystal structure.

Amorphous and quasicrystalline Zr₈₀Pt₂₀ and Zr₇₀Be₃₀ samples were prepared similarly. To obtain quasicrystalline samples, amorphous Zr₈₀Pt₂₀ and Zr₇₀Be₃₀ ribbons were annealed for 20 min at 600 and 650 K, respectively.

Extended X-ray absorption fine-structure (EXAFS) measurements were performed above the *K* absorption edges of zirconium (17 998 eV) and palladium (24 350 eV) and the *L*_{III} absorption edge of platinum (11 564 eV) on the A1 line at HASYLAB/DESY (Hamburg, Germany) at temperatures of 10, 77, and 300 K. The EXAFS spectra of thick single-crystal samples were measured with the use of the fluorescent technique, while the amorphous ribbons and quasicrystalline powders were ana-

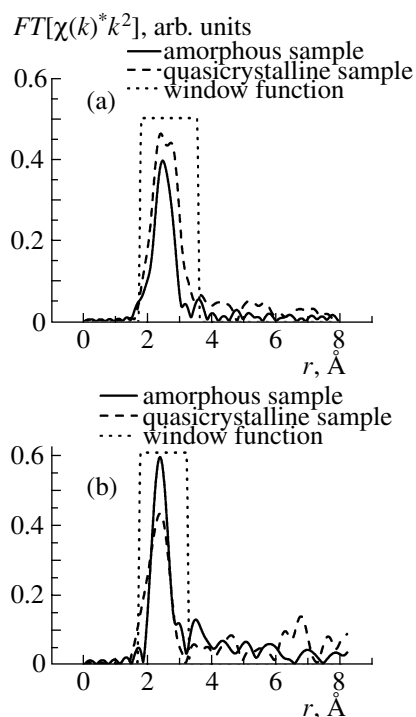


Fig. 1. Moduli of the Fourier transforms of the EXAFS function $\chi(k)k^2$ for the quasicrystalline and amorphous $Zr_{70}Pd_{30}$ samples, measured at $T = 10$ K above the K -absorption edges of (a) zirconium and (b) palladium. The rectangles show the inverse Fourier transform windows for selecting the contribution from the nearest zirconium and palladium environment.

lyzed in transmission. The EXAFS spectra were processed using the VIPER software package [5] using the standard selection procedure and Fourier analysis of the

EXAFS function $\chi(k)$; the amplitudes $f_j(\pi, k)$ and back-scattering phases $\phi_j(k)$ were calculated using the FEFF-8.20 program [6].

The EXAFS analysis of the local structure of zirconium and palladium in a $Zr_{70}Pd_{30}$ single crystal revealed that its similarity to the structure of the Zr_2Pd analog crystal [7], which was used to calculate the amplitudes and phases of this alloy in all three states. Figures 1a and 1b show the moduli of the Fourier transforms of the EXAFS functions for the quasicrystalline and amorphous $Zr_{70}Pd_{30}$ phases, measured above the K absorption edges of Zr and Pd, respectively. The shape of the Fourier transform modulus for the EXAFS function of a quasicrystal for the Zr K edge significantly differs from the Fourier transform modulus for the amorphous sample, which indicates the difference in the local structure of zirconium in the quasicrystalline phase from the structure in the amorphous state in view of the formation of icosahedral ordering; however, for the Pd K edge, the difference is not observed.

The results of the simulation of the EXAFS spectra for $Zr_{70}Pd_{30}$ are listed in Table 1; ordering around zirconium was modeled in two ways. The difference between the models is the introduction of an additional coordination sphere from one to two Zr atoms at a distance of 2.95 Å. Such a model provided a characteristic total coordination number of 11.5 atoms and somewhat more exactly described the experimental spectrum. In this case, the structure of the icosahedral cluster is distorted: most of Pd and Zr atoms are at distances of 2.70 and 3.18 Å, respectively; these values are in good agreement with the electron diffraction data [8]. The noted

Table 1. Parameters of the local structure of zirconium and palladium atoms in $Zr_{70}Pd_{30}$ in the quasicrystalline and amorphous states: the coordination number N , the interatomic distance R , and the Debye–Waller factor σ^2

| Absorption edge | Type of atom | N | $R, \text{Å}$ | $\sigma^2, \text{Å}^2$ |
|----------------------------------|--------------|----------------|---------------|------------------------|
| Quasicrystal $Zr_{70}Pd_{30}$ | | | | |
| K -Zr, model 1 | Pd | 1.6 ± 1.0 | 2.70 | 0.0071 |
| | Zr(1) | 2.35 ± 1.0 | 2.95 | 0.0200 |
| | Zr(2) | 7.4 ± 1.0 | 3.18 | 0.0151 |
| K -Zr, model 2 | Pd | 1.1 ± 1.0 | 2.70 | 0.0059 |
| | Zr | 6.4 ± 3.0 | 3.18 | 0.0147 |
| K -Pd | Zr | 3.9 ± 1.0 | 2.72 | 0.0122 |
| Amorphous phase $Zr_{70}Pd_{30}$ | | | | |
| K -Zr | Pd | 1.3 ± 1.0 | 2.73 | 0.0080 |
| | Zr | 2.3 ± 1.0 | 3.16 | 0.0124 |
| K -Pd | Zr | 2.9 ± 1.0 | 2.73 | 0.0077 |
| | Pd | 2.3 ± 1.0 | 2.83 | 0.0120 |

Table 2. Parameters of the local structure of $Zr_{80}Pt_{20}$ and $Zr_{70}Be_{30}$ in the quasicrystalline and amorphous states: the coordination number N , the interatomic distance R , and the Debye–Waller factor σ^2

| Absorption edge | Type of atom | N | $R, \text{Å}$ | $\sigma^2, \text{Å}^2$ |
|----------------------------------|--------------|----------------|-----------------|------------------------|
| Quasicrystal $Zr_{80}Pt_{20}$ | | | | |
| K -Zr | Zr-Pt | 1.6 ± 1.2 | 2.78 ± 0.09 | 0.0203 |
| | Zr-Zr(1) | 0.7 | 2.88 ± 0.02 | 0.0080 |
| | Zr-Zr(2) | 5.8 ± 2.3 | 3.18 ± 0.02 | 0.0182 |
| L_{3-} -Pt | Pt-Zr | 3.6 | 2.70 | 0.0103 |
| Amorphous phase $Zr_{80}Pt_{20}$ | | | | |
| K -Zr | Zr-Pt | 0.45 | 2.79 | 0.0036 |
| | Zr-Zr | 2.36 | 3.17 | 0.0130 |
| L_{3-} -Pt | Pt-Zr | 2.8 | 2.73 | 0.0078 |
| Quasicrystal $Zr_{70}Be_{30}$ | | | | |
| K -Zr | Zr-Zr(1) | 4.0 ± 3.0 | 2.93 ± 0.05 | 0.0179 |
| | Zr-Zr(2) | 10.5 ± 2.0 | 3.19 | 0.0123 |
| Amorphous phase $Zr_{70}Be_{30}$ | | | | |
| K -Zr | Zr-Be | 2.03 | 2.78 | 0.0060 |
| | Zr-Zr | 5.75 | 3.11 | 0.0192 |

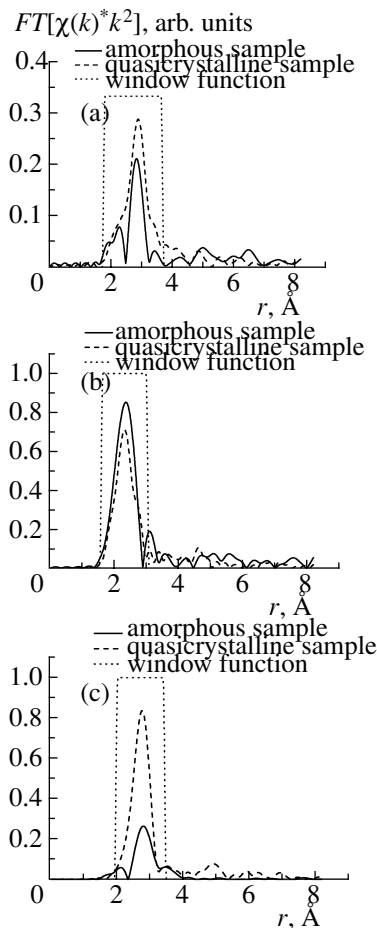


Fig. 2. Moduli of the Fourier transforms of the EXAFS function $\chi(k)k^2$ for the quasicrystalline and amorphous (a, b) $Zr_{80}Pt_{20}$ samples, measured at $T = 77$ K above the K -absorption edge of (a) zirconium and (b) platinum, and (c) $Zr_{70}Be_{30}$ samples, measured at $T = 77$ K above the Zr K -absorption edge. The rectangles show the inverse Fourier transform windows for selecting the contribution from the nearest zirconium and platinum environment.

distortion can be due to the fact that not all zirconium atoms are centers of icosahedral clusters in the quasicrystalline structure, and the EXAFS data reflect the averaged contribution of the local coordination of Zr atoms occupying different crystallographic positions. The formation of an icosahedral cluster is accompanied by a significant decrease in size of the first coordination spheres of Zr in comparison with a crystal. Palladium atoms are forced out from the Pd environment in the quasicrystalline phase.

The Zr local structure in the amorphous phase (Fig. 1a, Table 1) does not exhibit an icosahedral short-range order, although the electron diffraction data (obtained at sharp focusing of the electron beam into a nanosized spot) indicated the presence of icosahedral ordering regions. EXAFS spectroscopy does not make it possible to select such regions.

The EXAFS spectra of quasicrystalline and amorphous $Zr_{80}Pt_{20}$ above the Zr K - and Pt L_{III} -absorption

edges were processed in the same way as for $Zr_{70}Pd_{30}$. The structure of the main peak in the Fourier transform of EXAFS function, measured above the Pt L_{III} -absorption edge for a quasicrystal is the same as the structure of the amorphous phase peak. The results of the simulation of the EXAFS function $\chi(k)k^2$ on the basis of the β -ZrPt crystal model are listed in Table 2. This table contains also the data on simulation of the EXAFS function, measured above the Zr K -absorption edge of $Zr_{70}Be_{30}$. A quasicrystal is formed in both cases as for $Zr_{70}Pd_{30}$, and correlation of distances is observed. The nearest Pt environment turned out to include only four Zr atoms, located at a distance of 2.71 Å in the quasicrystalline phase, and three Zr atoms, located at a distance of 2.70 Å in the amorphous phase; Pt atoms were forced away from the local platinum structure in both cases. This arrangement can be related to the large radius and mass of platinum atoms. Icosahedral coordination is not formed around Pt. In $Zr_{70}Be_{30}$, an icosahedral cluster containing only Zr atoms is formed around zirconium, because Be atoms has a small radius and mass.

Thus, using EXAFS spectroscopy, we determined the character of local transformations of atoms in $Zr_{70}Pd_{30}$, $Zr_{80}Pt_{20}$, and $Zr_{70}Be_{30}$ binary alloys during transition to the quasicrystalline state. It is established that the centers of formation of icosahedral clusters in all three alloys are zirconium atoms. The local structure of palladium and platinum atoms is almost the same as in the amorphous phase. The distances to the nearest atoms correlate for these three materials; the differences in the structure are due to the differences in the size and mass of Pd, Pt, and Be atoms.

ACKNOWLEDGMENTS

We are grateful to the HASYLAB Program Committee for the possibility of carrying out experiments on the synchrotron source.

This study was supported by the Russian Foundation for Basic Research, project no. 05-02-16996-a.

REFERENCES

1. Shechtman, D., Blech, I., Gratias, D., and Cahn, J.W., *Phys. Rev. Lett.*, 1984, vol. 53, p. 1957.
2. Saida, J., Matsushita, M., and Inoue, A., *Intermetallics*, 2002, vol. 10, p. 1089.
3. Panova, G.Kh., Chernoplekov, N.A., and Shikov, A.A., *Fiz. Tverd. Tela* (St. Petersburg), 2005, vol. 47, no. 7, p. 1165 [*Phys. Solid State* (Engl. Transl.), vol. 47, no. 7, p. 1205].
4. Bancel, P.A., Heiney, P.A., Stephens, P.W., et al., *Phys. Rev. Lett.*, 1985, vol. 54, p. 2422.
5. Klementev, K.V., *J. Phys. D: Appl. Phys.*, 2001, vol. 34, p. 209.
6. Newville, M., Ravel, B., Haskel, D., et al., *Physica B*, 1995, vols. 208–209, p. 495.
7. Nakamura, T., *J. Non-Cryst. Solids*, 2002, vols. 312–314, p. 517.
8. Takagi, T., Ohkubo, T., Hirotsu, Y., et al., *Appl. Phys. Lett.*, 2001, vol. 79, p. 485.