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Valence band structure of i-ZnMgEr quasicrystal: photoemission study

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Abstract

The results of photoemission study of icosahedral single-grain ZnMgEr quasicrystals are presented. Synchrotron radiation photoemission measurements were performed on *in situ* cleaved samples at 10^{-10} mbar pressure and low, 140–150 K, temperature. The valence band photoemission spectra measured reveal a simple-metal type valence band of i-ZnMgEr with a distinct Fermi edge cutoff and a spectral feature at 0.7 eV below ε_F. Analysis of the PE spectra shows that the spectral feature observed corresponds to the van Hove singularities in the density of states, which are due to intersections of the Fermi surface with the 222100 and 311111 Bragg planes.

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

1. Introduction

The valence band structure of quasicrystals (QCs) is an important problem of their physics, because it is directly related to the problem of the nature of their electron states. Two main hypothetical schemes of the QC electronic structure can be distinguished. The first one is based on theoretical tight-binding linear-muffin-tin-orbital investigations (see e.g. [1]). The approach puts a stress on inapplicability of the Bloch theorem to quasicrystals, which might lead to the localized electron states. An alternative approach is based on the 'band structure hypothesis' [2, 3], which treats the electron subsystem as a nearly free-electron (NFE) gas affected by a weak quasicrystalline potential field

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{g}} V_{\boldsymbol{g}} \mathrm{e}^{\mathrm{i}\boldsymbol{g}\boldsymbol{r}}, \tag{1}$$

where $V_{\boldsymbol{g}}$ are the pseudopotentials and $\boldsymbol{g}$ are the reciprocal lattice vectors.

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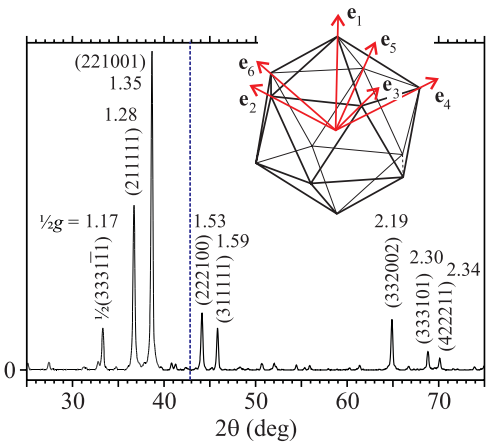

Figure 1. X-ray powder diffractogram of i-ZnMgEr quasicrystal. The indices of the diffraction peaks correspond to the reciprocal lattice vectors (2). The numbers at the peaks indicate the half moduli of the vectors in 10^8 cm^{-1} units. The dashed line corresponds to the Fermi wavevector $k_F = 1.49 \times 10^8$ cm^{-1}.

Here we present a photoelectron microspectroscopy study of single-grain icosahedral ZnMgEr quasicrystals, which shows that the i-ZnMgEr valence band in the vicinity of the Fermi level and below it down to about 4 eV is predominantly due to the sp derived electron states, i.e. is of the simple-metal type (contrary to the valence bands of most other quasicrystals, which are dominated by d electrons [4]). The electronic structure of i-ZnMgEr can be successfully modelled within a framework of the band structure hypothesis. The i-ZnMgEr electron energy spectrum in the vicinity of the Fermi level is determined by the Fermi surface intersections with the 222100 and 311111 families of Bragg planes.

2. Experiment

The icosahedral $Zn_{65}Mg_{24}Er_{11}$ single-grain quasicrystals were grown by the liquid-encapsulated top-seeded solution-growth method (described in [5] for the growth of i-ZnMgY). The structural perfection of the grown QCs was confirmed by the sharp, resolution limited, Bragg peaks of their diffraction patterns. The experimental powder x-ray Cu Kα diffractogram recorded by a Siemens D500 diffractometer is presented in figure 1. The six-dimensional indices m_i ($i = 1, 2, \ldots, 6$) of the diffraction peaks correspond to indices of the reciprocal lattice vectors

$$\boldsymbol{g} = \frac{2\pi}{a} \sum_{i=1}^{6} m_i \boldsymbol{e}_i, \tag{2}$$

where $\boldsymbol{e}_i$ are the unit vectors of an icosahedron (inset to figure 1) and $a = 5.18$ Å is the quasilattice constant. The numbers at the diffraction peaks in figure 1 indicate the half moduli of the reciprocal lattice vectors, $\frac{1}{2}g$, in 10^8 cm^{-1} units. The mass density of i-ZnMgEr was measured by a Micrometrics AccuPyc 1330. The recorded value $\varrho = 5.87 \pm 0.033$ g cm^{-3} corresponds to the atomic concentration $n_a = 5.30 \times 10^{22}$ cm^{-3}.

Photoemission (PE) measurements were performed with an angle-resolved scanning photoelectron microscope, at beamline BL31 of the Swedish Synchrotron-Radiation Facility MAX-lab (Lund). The single-grain specimens for the PE measurements were prepared in a form of small, ≈0.5 cm long, rods with ≈1 mm^2 cross section. The samples were cleaved *in situ* at 2×10^{-10} mbar and low, 140–150 K, temperature. The incident photon beam was focused to the 1.5 μm spot on the cleaved, predominantly C_5, sample surface at normal incidence, and PE spectra were recorded with a VG CLAM2 analyser mounted at 47.5°.

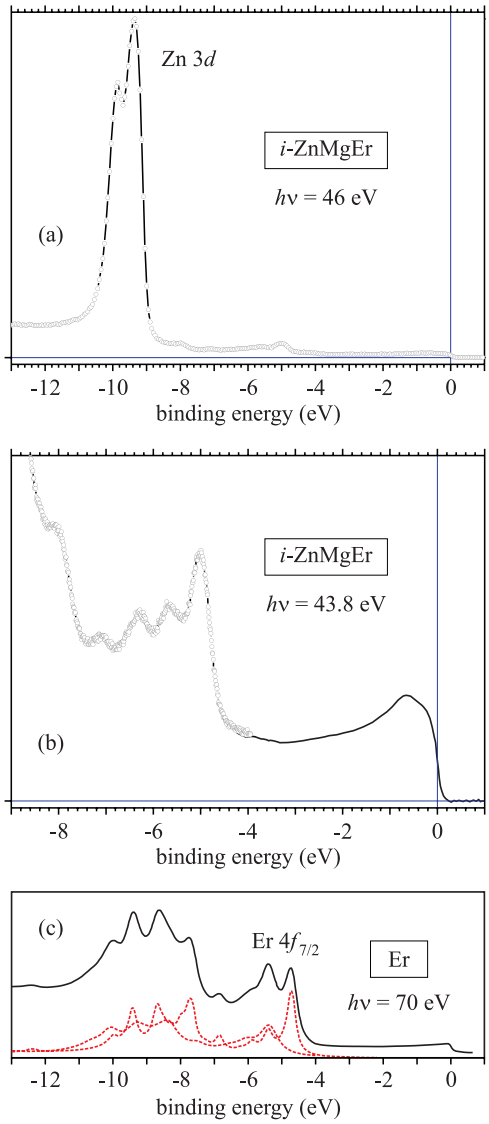

Figure 2. Valence band PE spectra of i-ZnMgEr (T = 150 K) quasicrystal (a) and (b), and the Er 4f PE line in pure erbium [7] (c).

Though the cleaved surfaces were geometrically rough, no significant changes in the i-ZnMgEr PE spectra were observed when they were recorded from various spots of the cleaved surface, nor when they were recorded from various specimens of a series of cleaved samples. The cleanliness of the cleaved surfaces was routinely monitored following photoemission from the O 2p states [6].

3. Results and discussion

The experimental valence band (VB) photoemission spectra of i-ZnMgEr, recorded at about 45 eV incident photon energy and 150 K, are presented in figures 2(a) and (b). As seen, the valence band bottom is dominated by the Zn 3d shallow core level doublet. The broad complex structure at binding energies of about 6 eV is due to the Er $4f_{7/2}$ states, as can be easily identified from a comparison with the PE spectrum of pure erbium [7] presented in figure 2(c).

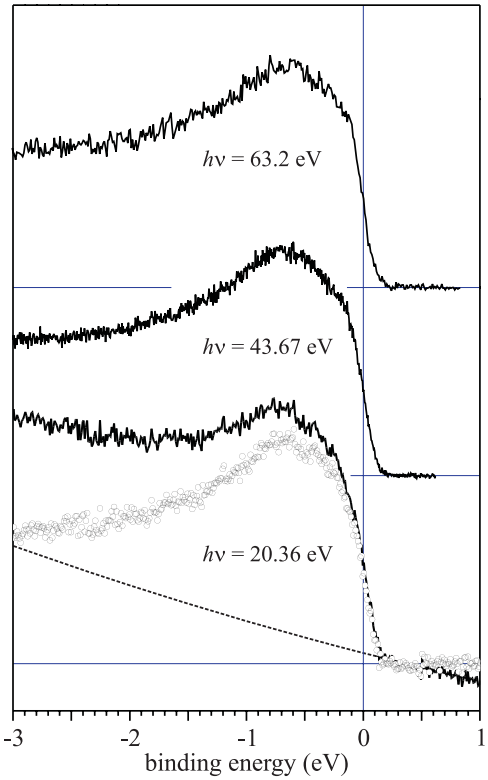

Figure 3. Experimental i-ZnMgEr valence band PE spectra above Er 4f levels recorded at various photon energies (full curves). The dashed curve indicates the background of the 20.36 eV spectrum and the dots correspond to the background-subtracted spectrum.

The PE valence band spectra above the Er 4f line (see figures 2(b) and 3) show a clear metallic Fermi edge and a spectral feature below the Fermi level. The spectral intensity exhibits a maximum at ≈0.7 eV below the Fermi level and a subsequent decrease as ε_F is approached. As seen from figure 3, the valence band spectra in the vicinity of the Fermi level and below it down to Er $4f_{7/2}$ line have not changed in their spectral shape while recording the spectra at different photon energies in the interval of 20–60 eV. Additionally, the i-ZnMgEr VB spectrum in the interval of binding energies down to about 4 eV is rather close to the VB spectra of i-ZnMgY and i-ZnMgHo quasicrystals [8]. This allows us to conclude that the i-ZnMgEr VB at the Fermi level and below it down to about 4 eV is determined primarily by the s (or sp) derived electron states.

Assuming that the electron energy spectrum of the quasicrystal can be treated within a framework of the band structure hypothesis, one expects the energy spectrum to be considerably affected by intersections of the Fermi surface with the Bragg planes. The Fermi wavevector of i-ZnMgEr can be calculated as $k_F = (3\pi^2 n)^{1/3}$, where $n = \overline{Z} n_a$ is the electron concentration and $\overline{Z} = 2.11$ is the average valence of i-ZnMgEr atoms. The $k_F = 1.49 \times 10^8$ cm^{-1} wavevector estimated, as seen from figure 1, lies in a close proximity to 222100 and 311111 Bragg planes. Sixty equivalent 222100 Bragg planes and twelve 311111 ones make up the effective Brillouin zone, alias the Jones zone, of the i-ZnMgEr quasicrystal which is depicted in figure 4. As is known from the usual NFE analysis, intersections of the electron isoenergetic surface with the Brillouin zone open the pseudogaps $\Delta_g = 2|V_g|$ in the energy spectrum and lead to van Hove singularities in the density of states.

The density of states $R(\varepsilon)$ within the framework of the NFE model can be calculated analytically [8]. A possible intrinsic broadening of the electron states was taken into account by

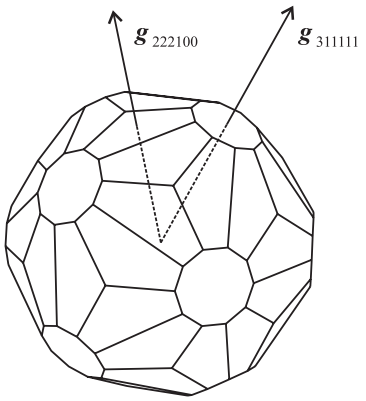

Figure 4. The 222100 and 311111 Jones zone.

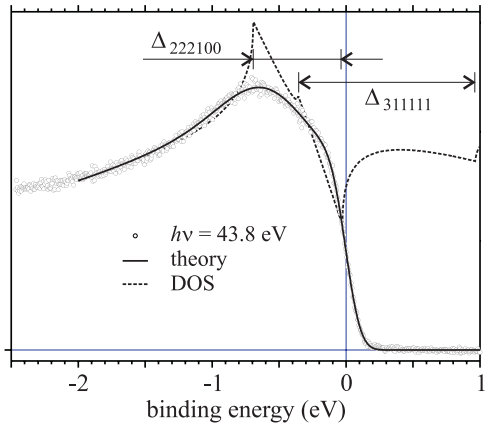

Figure 5. Near Fermi-edge PE spectrum of i-ZnMgEr ($T = 150$ K).

Gaussian convolution of the van Hove singularities. Finally, the calculated DOS was multiplied by the Fermi–Dirac distribution function $f(\varepsilon)$ and the near Fermi-edge PE spectral intensity was simulated as a convolution of the $R(\varepsilon)f(\varepsilon)$ product with the experimental resolution Gaussian function. The results of the calculations are presented by the full curve in figure 5. As is seen, the theoretical model nicely reproduces the experimental data. (The theoretical curve in the figure overlaps with the experimental data presented by open dots.)

The dashed curve in figure 5 presents the reconstructed DOS. As is seen, the feature of the PE spectrum at ≈0.7 eV below the Fermi level is due first of all to the Δ_{222100} pseudogap, located below the Fermi level, and is affected by the lower edge of the Δ_{311111} pseudogap. The van Hove singularities of the density of states, which correspond to edges of the pseudogaps, are smoothed in the experimental PE spectra due to the finite instrumental energy resolution and the intrinsic broadening.

The best fit of the theoretical and experimental PE spectral intensities by the least-squares technique has been obtained at a 0.2 eV value of the instrumental energy resolution, which corresponds to the nominal energy resolution of the PE microscope used. The deduced parameters of the i-ZnMgEr energy spectrum, the pseudogap widths Δ_{222100} and Δ_{311111}, the intrinsic broadening Γ, and the position of the Fermi level ε_F with respect to VB bottom, are presented in table 1. The error interval for the parameters determined is about 20% as estimated upon analysing PE spectra, recorded at various photon energies and from various specimens of a series of cleaved samples.

Table 1. Energy spectrum parameters of i-ZnMgRE quasicrystals.

	Δ_{222100} (eV)	Δ_{311111} (eV)	Γ (eV)	ε_F (eV)
i-ZnMgY[a]	0.63	1.16	0.23	9.31
i-ZnMgHo[a]	0.61	0.98	0.22	9.32
i-ZnMgEr[b]	0.64	1.25	0.24	9.32

[a] Reference [8].
[b] This work.

The values of the i-ZnMgEr electron energy spectrum parameters deduced are similar to those determined previously for i-ZnMgY and i-ZnMgHo quasicrystals [8] (see table 1). The pseudogap widths of i-ZnMgRE quasicrystals, $\Delta_{222100} \approx 0.6$ eV and $\Delta_{311111} \approx 1$ eV, correspond to the pseudopotential values $|V_{222100}| \approx 0.3$ eV and $|V_{311111}| \approx 0.5$ eV, which are comparable with pseudopotentials of the usual simple-metals [9]. The broadening parameter of the electron states $\Gamma \approx 0.2$ eV corresponds to the lifetime $\tau = \hbar/\Gamma \approx 3 \times 10^{-15}$ s, which is an order of magnitude shorter than the relaxation time in pure Zn and Mg metals at 77 K. This is in accord with the well known experimental fact that relaxation times in quasicrystals are essentially shorter than in the usual crystalline metals.

Summarizing, we conclude that the photoemission spectra of the icosahedral ZnMgEr quasicrystal show the i-ZnMgEr valence band in the vicinity of the Fermi level and below it down to about 4 eV to be of the simple-metal type, originating predominantly from the sp-electron states. The electron energy spectrum near the Fermi level is determined by intersections of the Fermi surface with the 222100 and 311111 Bragg planes. Due to the high icosahedral symmetry and, consequently, to the high multiplicity of the intersections, a distinct van Hove structure manifests itself in the density of states near ε_F. The parameters of the i-ZnMgEr electron energy spectrum deduced from an analysis of PE spectra are similar to those previously determined for i-ZnMgY and i-ZnMgHo quasicrystals.

Acknowledgments

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