Lithuanian Journal of Physics, Vol. **47**, No. 4, pp. 429–433 (2007) doi:10.3952/lithjphys.47402

THE Mg 2*p* CORE-LEVEL IN Zn_2Mg *

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Received 12 June 2007; revised 14 September 2007; accepted 21 November 2007

We present a synchrotron radiation photoemission (PE) spectroscopy study of the Mg 2*p* shallow core-level in Zn_2Mg Laves phase. The PE measurements were performed on *in situ* cleaved single-grain samples at 10^{-10} mbar pressure and low, 90−100 K, temperature. Analysis of Mg 2*p* PE spectra indicates the surface shift of the core-level of −0.12 eV. Parameters of the bulk component of Mg 2*p* level, the binding energy of 49.98 eV, the spin-orbit splitting $\Delta_{s-o} = 0.28$ eV, and the lifetime broadening $\gamma = 0.06$ eV, are comparable to their values determined previously for pure crystalline Mg.

Keywords: intermetallic compounds, photoemission spectroscopy, shallow core-levels

PACS: 71.20.Lp

1. Introduction

The present paper aims at a detailed analysis of the photoemission spectra of Mg 2*p* shallow core-level in Zn_2Mg.

Magnesium dizinc is an intermetallic hexagonal crystalline compound ($a = 5.233$ Å, $c = 8.566$ Å [1]) of the Laves phase. The primitive cell of Zn_2Mg Laves phase contains twelve atoms, eight zinc atoms of which occupy two inequivalent sites, Zn1 (six Zn atoms) and Zn2 (two Zn atoms), while all four magnesiums atoms are in equivalent sites (the atomic surrounding of Mg sites is illustrated in Fig. 1).

The atomic composition of Zn_2Mg and local neighbouring surrounding of its atoms are similar to those in icosahedral fci-$Zn_{60}Mg_{30}RE_{10}$ quasicrystals, and magnesium dizinc presents a convenient physical reference system for studies of both the atomic [2, 3], and the electronic [4] structure of the fci-ZnMgRE quasicrystals.

Recently we have revealed that the local atomic surrounding of fci-ZnMgRE quasicrystals affects the Mg 2*p* shallow core-level and can be traced in photoemission spectra [5]. The detailed analysis [6] requires a knowledge of the Mg 2*p* core-level parameters, especially its lifetime broadening, which in solids is determined by the radiative or the Auger electron transitions from the valence band to the level. Since an action of an atomic surrounding in metallic solids can be treated as a small perturbation both for core-levels and for the valence band states, one can assume that the lifetime broadening does not essentially depend on the surrounding and is an intrinsic characteristic of a core-level.

2. Experiment

The single-grain Zn_2Mg crystals investigated were grown by the liquid-encapsulated top-seeded solution growth technique [7]. The quality of the crystals was checked by Laue photography.

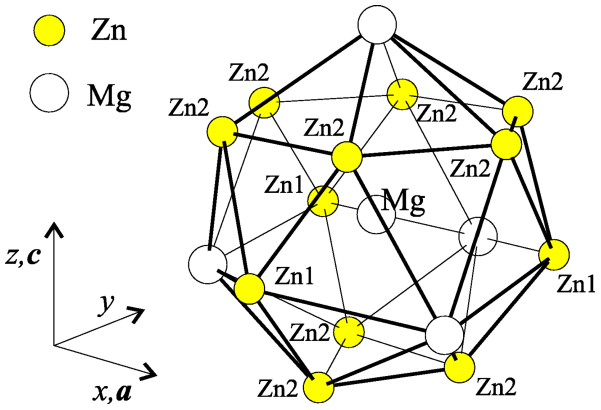

Fig. 1. The coordination polyhedron of magnesium site.

* The report presented at the 37th Lithuanian National Physics Conference, 11–13 June 2007, Vilnius, Lithuania.

ISSN 1648-8504

The PE measurements were performed at beamline BL31 of the Swedish synchrotron radiation facility MAX-lab (Lund). The Zn_2Mg samples for PE measurements were prepared in a form of small, ≈0.5 cm long, rods with ≈1 mm^2 cross-section and were cleaved *in situ* at $2{\cdot}10^{-10}$ mbar and low, 90− 100 K, temperature. The PE spectra were recorded with the VG CLAM2 analyser mounted at 47.5°. The instrumental energy resolution was about 0.07−0.25 eV. It varied depending on the photon energy ($h\nu = 60-120$ eV) and the chosen pass energy of the analyser.

Though the cleaved surfaces were geometrically rough and we could not control a crystallographic orientation of the cleaved surfaces, no significant changes in PE spectra were observed when they were recorded from various spots of the cleaved surfaces, neither when they were recorded from various specimens of a series of cleaved samples.

3. Results and discussion

3.1. PE spectra

The raw experimental Mg $2p$ PE spectra recorded were multiplied by the kinetic energy ε_{kin} of photoelectrons to eliminate the inverse ε_{kin} dependence of the electron transmission of the analyser used, and the secondary electron background of the spectra was subtracted making use of the Shirley step algorithm [8] or, for the $h\nu \sim$60 eV PE spectra, by the polynomial algorithm (see, e. g., Ref. [9]).

The photoemission spectra of Mg $2p$ core-level in magnesium dizinc, recorded at different photon energies, are presented in Fig. 2.

The spectra at low (61 and 73 eV) photon energy show a clear, distinct spin-orbit doublet structure of the Mg $2p$ level with the theoretical statistical value of the branching ratio $I_{p_{3/2}}/I_{p_{1/2}} = 2$. The Mg $2p$ spectra recorded at higher photon energies indicate changes in the spectral shape of PE line. The spectra can be well approximated by two spin-orbit doublets, which correspond to the bulk and surface components of Mg $2p$ level.

Components of Mg $2p$ core-level were modelled by the Doniach–Šunjić (DS) lines [10]

$$F_{\text{DS}}(\varepsilon) = \Gamma(1-\alpha)\,\frac{\cos\left[\dfrac{\pi\alpha}{2} + (1-\alpha)\,\text{atan}\dfrac{\varepsilon-\varepsilon_i}{\gamma}\right]}{\left[\gamma^2 + (\varepsilon-\varepsilon_i)^2\right]^{(1-\alpha)/2}}\,, \tag{1}$$

where ε_i is the binding energy of the component, γ is the lifetime broadening parameter, and α is the asymmetry parameter.

The PE spectral intensity of Mg $2p$ level was simulated as the convolution

$$I(\varepsilon) = \int_{-\infty}^{\infty} \mathrm{d}\varepsilon'\, F(\varepsilon') G(\varepsilon' - \varepsilon)\,, \tag{2}$$

where $F(\varepsilon')$ is a superposition of four DS lines (1), which correspond to the bulk and the surface spin-orbit doublets, and $G(\varepsilon' - \varepsilon)$ is the Gaussian function, which accounts for the instrumental and thermal broadening of PE spectra,

$$G(\varepsilon' - \varepsilon) = \frac{1}{\sqrt{2\pi}\,s}\,\mathrm{e}^{-(\varepsilon'-\varepsilon)^2/(2s^2)}\,. \tag{3}$$

Here s is the standard deviation of the Gaussian function, which is related with a full width at half-maximum of the Gaussian curve as $\text{FWHM}_{\text{G}} = \sqrt{8\,\ln 2}\,s$. At the low temperatures investigated, the s parameter is primarily determined by the overall energy resolution of the PE set-up used.

Results of the Mg $2p$ PE spectral intensity calculations are presented by full curves in Fig. 2 and, as seen, nicely fit experimental data.

The parameters of the core-level – the weighted centre of the bulk spin-orbit doublet ε_0, the spin-orbit splitting $\Delta_{\text{s-o}}$, the surface shift Δ_{s}, the lifetime broadening of the bulk and surface components γ and γ_{s}, and the asymmetry parameter α – have been deduced by the least-squares technique and are presented in Table 1 together with literature data [11, 12] for the Mg $2p$ level in pure magnesium metal.

The values of the standard deviation of the Gaussian (3) deduced by the least-squares technique coincide with nominal values of the instrumental energy resolution of the photoemission set-up used [13] with an accuracy of 30% for 40 PE spectra examined. This is a sound support of a reliability of the deduced Mg $2p$ level parameters.

The parameters of the bulk spin-orbit doublet in Zn_2Mg, the binding energy of 49.98 eV, the spin-orbit splitting $\Delta_{\text{s-o}} = 0.28$ eV, and the lifetime broadening $\gamma = 0.06$ eV, as seen from Table 1, are comparable with their values in pure Mg metal [11, 12].

The asymmetry parameter α of Mg $2p$ PE line in Zn_2Mg, which was assumed to be the same for the bulk and surface components, depends on the photon energy. The parameter steeply changes (see Fig. 3(a)) from $\alpha \approx 0$ to $\alpha \approx 0.1$ values at the photon energy of about 65 eV, i. e. at ≈15 eV above the photoioniza-

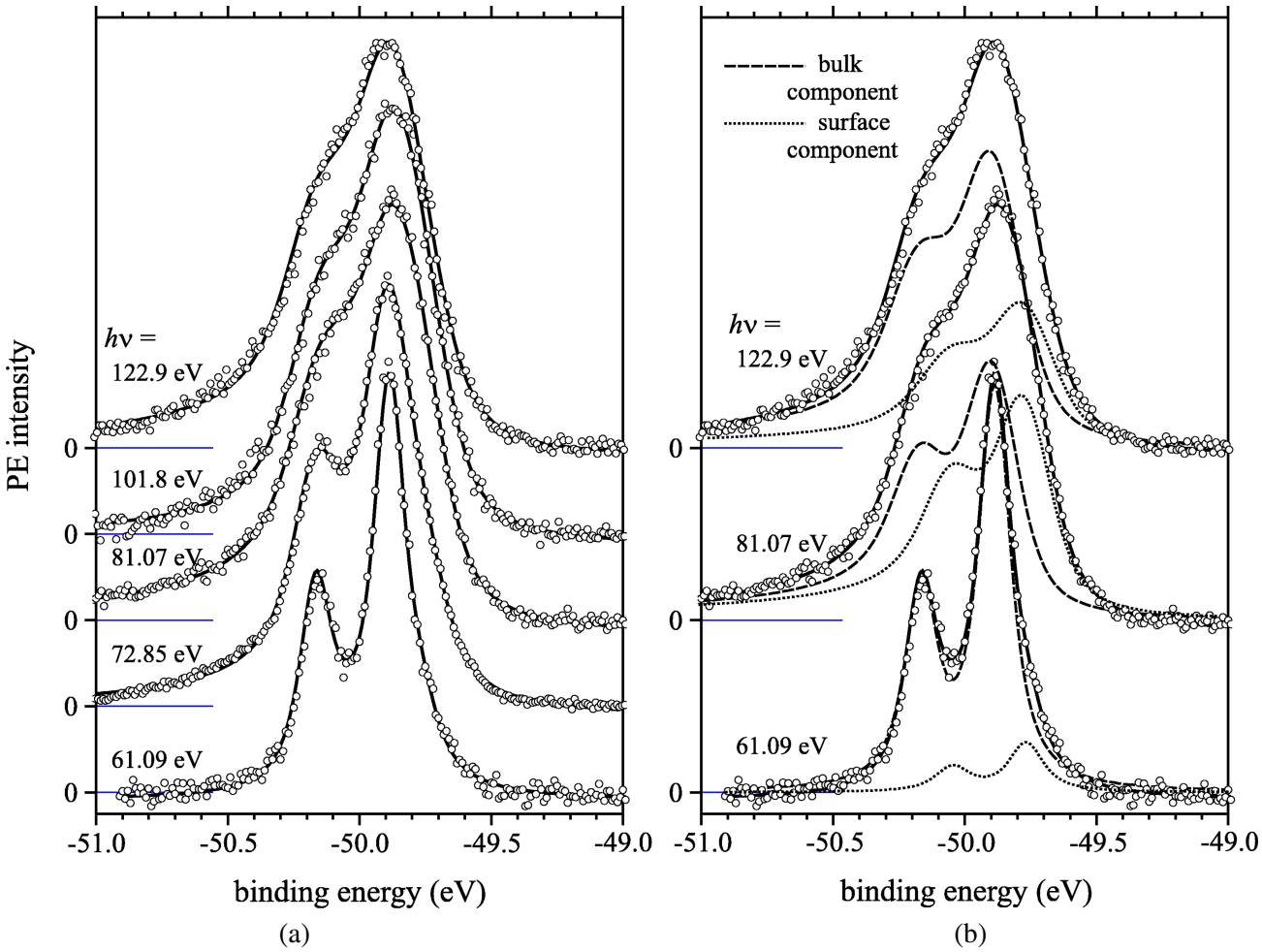

Fig. 2. PE spectra of Mg $2p$ shallow core-level in crystalline Zn_2Mg ($T = 90-100$ K). Dots and curves present experimental and theoretical data, respectively. Dashed and dotted curves in (b) correspond to the bulk and surface components.

Table 1. Comparison of parameters of the Mg $2p$ level in Zn_2Mg (results of the present study) with their values in pure crystalline magnesium (literature data [11, 12]).

	Zn_2Mg	Mg
ε_0 (eV)	-49.98	-49.60^a
Δ_{s-o} (eV)	0.28	0.28^b
Δ_s (eV)	-0.12	0.14^a
γ (eV)	0.06	0.03^a
γ_s (eV)	0.07	0.05^a
α	$\approx 0^c$ $\approx 0.1^d$	$0.13^{b,e}$

[a] Ref. [12].
[b] Ref. [11].
[c] For $h\nu < 65$ eV.
[d] For $h\nu > 65$ eV.
[e] For $h\nu \approx 1.5$ keV.

tion threshold. The jump of the asymmetry parameter can be due to changes from the adiabatic to the sudden regime of Mg $2p$ photoionization and can be related with polarization effects of Zn $3d$ electrons, the binding energy of which (with respect to the vacuum level) is ≈ 14 eV. Here we follow the interpretation of the effect suggested by Himpsel et al. [14], who observed the $\Delta\alpha = 0.09$ jump at 14 eV above photothreshold for Zn $3p$ core-level in pure metallic zinc by analysing the Zn $M_3M_{4,5}M_{4,5}$ Auger lines.

The determined surface shift $\Delta_s = -0.12$ eV of Mg $2p$ core-level in Zn_2Mg is comparable in its absolute value with that determined for pure magnesium [12], $\Delta_s = 0.14$ eV.

3.2. Electron inelastic mean free path

As seen from Fig. 2(b), the ratio of the bulk and surface s-o doublets presented by dashed and dotted curves depends on the photon energy and, therefore, on the kinetic energy of photoelectrons. The kinetic energy dependence of the bulk-to-surface ratio $\beta(\varepsilon_{kin})$, which was deduced from the decomposition of experimental Mg $2p$ PE spectra, is presented in Fig. 3(b).

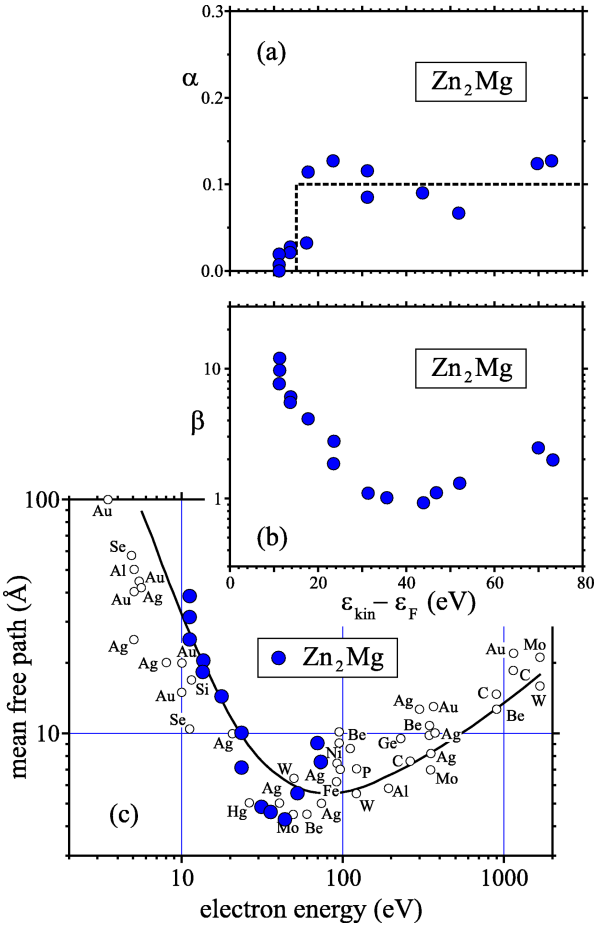

Fig. 3. Dependence of (a) the asymmetry parameter and (b) the ratio of Mg $2p$ bulk and surface components on the electron kinetic energy. (c) Inelastic mean free path versus the electron energy. Full dots correspond to Zn_2Mg. Open dots correspond to literature data [15] for pure elemental crystals.

The bulk-to-surface ratio β is related with the electron inelastic mean free path λ as

$$\lambda = \frac{d}{\ln(1+\beta^{-1})}\,, \qquad (4)$$

where d is the distance between atomic layers. If the two s-o doublets of Mg $2p$ indeed correspond to the surface and bulk components of the level, the electron inelastic mean free path dependence on the kinetic energy, $\lambda(\varepsilon_{\rm kin})$, should follow the so-called "universal curve" of electron escape depths, which is presented by full curve in Fig. 3(c). The full dots in the figure represent the inelastic mean free path (4) in Zn_2Mg, which was calculated from the determined β values and assuming the d parameter to be equal to a double average interatomic distance in Zn_2Mg, $d = 2r_{\rm a} = 2\sqrt[3]{3/(4\pi n_{\rm a})} = 3.2$ Å (where $n_{\rm a}$ is the atomic concentration). As seen from Fig. 3(c), the inelastic mean free path in magnesium dizinc indeed follows the "universal curve" and is in a good agreement with literature data [15] for pure elemental crystals (open dots in Fig. 3(c)).

3.3. Summary

The presented analysis of photoemission spectra of the Mg $2p$ shallow core-level in the Zn_2Mg Laves phase reveals the surface shift of the level of -0.12 eV.

Parameters of the bulk component of Mg $2p$ level, the binding energy of 49.98 eV, the spin-orbit splitting of 0.28 eV, and the lifetime broadening of 0.06 eV, are comparable to their values in pure crystalline Mg.

Acknowledgement

Support by the EC Access to Research Infrastructure programme is gratefully acknowledged.

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Mg 2*p* ATOMINIS LYGMUO Zn_2Mg

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Santrauka

Magnio dicinkas yra heksagoninis Laves fazės kristalas, kurio atominė sudėtis ir atomų išsidėstymas yra panašūs kaip paviršiuje centruotuose ikosaedriniuose fci-ZnMgRE kvazikristaluose.

Pateikti Zn_2Mg atominio Mg $2p$ lygmens fotoemisinių (PE) matavimų ir teorinio modeliavimo rezultatai, atskleidžiantys paviršinį lygmens poslinkį. Fotoemisiniai tyrimai buvo atlikti sinchrotroninės spinduliuotės laboratorijoje MAX-lab (Lundas) BL31 fotoelektroniniu mikroskopu. Monokristaliniai Zn_2Mg bandiniai buvo nuskelti ir PE matavimai atlikti ypač didelio vakuumo, 10^{-10} mbar, ir žemos temperatūros, 90–100 K, aplinkoje. Skiriamoji naudotos aparatūros geba 0,07–0,25 eV, tirtas spektrinis intervalas $h\nu = 60$–130 eV.

Eksperimentiniai Mg $2p$ lygmens PE spektrai, išmatuoti esant santykinai mažoms, $h\nu \approx 60$ eV, fotono energijoms, demonstruoja akivaizdžiai išreikštą s-o dubletinę lygmens sandarą. Lygmens parametrai – ryšio energija 49,98 eV, s-o suskilimas 0,28 eV ir baigtinės gyvavimo trukmės sąlygotas išplitimas 0,06 eV – yra artimi šių parametrų vertėms kristaliniame magnyje. Didėjant fotonų energijai, $h\nu > 60$ eV, Mg $2p$ PE linijos spektrinė forma kinta. Spektrų analizė rodo, kad PE atsaką sudaro du s-o dubletai, atitinkantys tūrinį ir paviršinį Mg $2p$ lygmens sandus. Nustatytas paviršinis lygmens poslinkis yra $-0{,}12$ eV.

Analizuojant tūrinio ir paviršinio s-o dubletų intensyvumų santykio priklausomybę nuo kinetinės elektronų energijos ε_{kin}, atskleista Zn_2Mg elektronų neelastinio vidutinio laisvojo kelio $\lambda(\varepsilon_{\text{kin}})$ priklausomybė, kuri gerai dera su literatūroje randamomis elementariųjų kristalų λ vertėmis.