Anomalous transport properties of the half-metallic ferromagnets Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn

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In this work, the theoretical and experimental investigations of Co$_2$Ti$^Z$ ($Z =$ Si, Ge or Sn) compounds are reported. Half-metallic ferromagnetism is predicted for all three compounds with only two bands crossing the Fermi energy in the majority channel. The magnetic moments fulfil the Slater–Pauling rule and the Curie temperatures are well above room temperature. All compounds show a metallic-like resistivity for low temperatures up to their Curie temperature, above the resistivity changes to semiconducting-like behaviour. A large negative magnetoresistance (MR) of 55 per cent is observed for Co$_2$TiSn at room temperature in an applied magnetic field of $\mu_0 H = 4\, T$, which is comparable to the large negative MRs of the manganites. The Seebeck coefficients are negative for all three compounds and reach their maximum values at their respective Curie temperatures and stay almost constant up to 950 K. The highest value achieved is $-52\, \mu V K^{-1}$ for Co$_2$TiSn, which is large for a metal. The combination of half-metallicity and the constant large Seebeck coefficient over a wide temperature range makes these compounds interesting materials for thermoelectric applications and further spinocaloric investigations.

Keywords: half-metallic ferromagnets; electronic structure; Heusler compounds; thermoelectric properties

1. Introduction

In the last few years, Heusler alloys have attracted a lot of interest as suitable materials for spintronic applications [1]. A huge amount of theoretical and experimental studies investigating the half-metallic properties and enhancing the performance of compounds and devices for different types of applications were carried out. In 2005, Hashemifar et al. [2] showed in a density functional

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theory study the possibility of preserving half-metallicity at the surface of the Heusler compound Co$_2$MnSi(001). More recently, Shan et al. [3] demonstrated experimentally the half-metallicity of Co$_2$FeAl$_{0.5}$Si$_{0.5}$ at room temperature. The ability to grow well-ordered half-metallic Heusler thin films on semiconductors (e.g. Ge (111)) makes Heusler compounds suitable for spin injection, as shown by Hamaya et al. [4]. The transport properties of pure and doped Fe$_2$VAl show semiconductor-like behaviour with interesting and anomalous features near the structural transition temperature, with an increasing absolute Seebeck coefficient with increasing temperature [5,6]. The recent observation of the spin Seebeck effect allows a pure spin current to be passed over a long distance [7] and is directly applicable to the production of spin-voltage generators that are crucial for driving spintronic devices [8–10]. To generate effectively a spin current, and for other spincaloric applications as well, one needs half-metals with constant Seebeck effect behaviour [11]. A constant Seebeck effect in temperature dependence is found especially in correlated systems such as pure and doped SrRuO$_3$ [12]. It can also be achieved, e.g. in PbTe crystals, with a sophisticated and experimentally complex graded indium doping through the crystal [13]. This report will show that the Heusler compounds Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn combine all the requirements of half-metallic ferromagnets with a constant Seebeck coefficient that can be used in future for spincaloric devices. A big advantage is the easy tunability of the properties of the Heusler compounds, which makes it easy to design new materials [14,15].

2. Computational details

The electronic structure of the compounds was calculated by means of the full potential linearized augmented plane wave (FLAPW) method [16,17]. Details of the calculations are reported in Kandpal et al. [18]. The calculated band structure of Co$_2$TiGe is shown in figure 1. A band gap in the minority states occurs at the Fermi energy $\varepsilon_F$. This minority gap is characteristic for half-metallic materials, as was previously shown by various authors [18–22]. The size of the minority band gap amounts to $\Delta E_{\text{HMF}} = 500$ meV and the Fermi energy is located close to the minimum of the conduction band. This was confirmed by the experimental investigation of the spin-resolved unoccupied density of states [23]. The majority band structure is metallic with only two bands crossing $\varepsilon_F$ and an electronic instability (van Hove singularity) close to the $L$ point just below $\varepsilon_F$. Owing to the band gap in the minority states the magnetic moment is an integer and has a value of exactly 2 $\mu_B$ for the primitive cell. A closer analysis shows that the magnetic moment is located at the Co atoms only. This means that each of the two Co atoms in the primitive cell carries a magnetic moment of 1 $\mu_B$.

3. Experimental details

The Co$_2$TiZ samples were produced by arc melting of stoichiometric amounts of the elements, followed by annealing in evacuated quartz tubes for 21 days. For more details about the sample preparation see [24].
Figure 1. Spin-resolved electronic structure of Co$_2$TiGe. Shown are the band structures for the (a) majority and (c) minority electrons together with the (b) density of states. (Online version in colour.)

The crystalline structure of the compounds was investigated by X-ray powder diffraction (XRD) using Mo-K$_\alpha$ radiation (Bruker D8 Advance). Complementary, temperature-dependent XRD experiments were performed using the XRD beamline at the bending magnet D10 of the Brazilian Synchrotron Light Laboratory (LNLS). For details about the characteristics of the beamline see [25].

The magnetic properties of the Co$_2$TiZ samples were investigated by a superconducting quantum interference device (SQUID; Quantum Design MPMS-XL-5).

To inspect the surface, a scanning electron microscope (SEM; Jeol JSM-6400) equipped with an energy dispersive X-ray (EDX) detection system (Surface Concept GmbH) was used. The samples were measured under a vacuum of $3 \times 10^{-6}$ mbar. An acceleration voltage of 20 kV was applied and an inspection angle of $35^\circ$ was set up. For the correction, the ZAF method was applied. A Digital Image Processing System (DIPS) was used for image acquisition and the program WINEDS v. 4.0 was used for the quantitative chemical analysis.

For the HAXPES investigation, the sample bars were cleaved in situ. This ensures that the samples are free of oxygen contamination. The HAXPES experiments were performed using the beamline BL15XU at SPring-8 (Japan). The photon energy was fixed at 5.947 keV using a double crystal monochromator and a Si(333) post-monochromator. The photoemitted electrons were analysed for their kinetic energy and detected by means of a hemispherical analyser (Scienta). The overall energy resolution (monochromator plus analyser) was set to 250 meV, as verified by spectra of the Au valence band at the Fermi energy. The angle between the electron spectrometer and the photon propagation is fixed at $90^\circ$. The photons are $p$-polarized, that is, the electric field vector is in the plane of incidence and always pointing in the direction of the electron detector. A near-normal emission ($\theta = 8^\circ$) detection angle was used.
This corresponds to an angle of incidence of $\alpha = \theta - 90^\circ = 82^\circ$. One should note, however, that these angles might not be that sharply defined for the cleaved samples, but rather vary across the area of the light spot owing to surface roughness.

The measurements of the transport and thermoelectric properties were carried out with a Physical Property Measurement System (Model 6000, Quantum Design) on bars of about $2 \times 2 \times 8 \text{mm}^3$, which were cut from the pellets and polished before measurement. The resistivity data for temperatures from 2 K to 400 K were obtained by a standard AC four-probe method and the data from 350 to 950 K were measured by a standard DC four-point method.

The X-ray absorption spectroscopy experiments were performed using the UE56/1-SGM beamline at the German synchrotron light source BESSY II. The samples were fractured in situ under an ultra-high vacuum ($p = 1 \times 10^{-9} \text{Torr}$) directly before measurement. X-ray absorption was measured by the total electron yield (TEY). The sample was shielded by a conducting tube in order to collect all electrons. An external magnetic field of 1.22 T was applied along the direction of the incident X-ray beam, i.e. approximately perpendicular to the fractured sample surface, and switched after each datum point to determine the X-ray circular dichroism (XMCD) signal while the polarization was kept constant. The energy resolution of the X-ray monochromator was set to ca 0.4 eV at 800 eV.

4. Results and discussion

(a) Structure and composition

The crystal structure of the samples was investigated by XRD using Mo-K$_\alpha$ as well as synchrotron radiation. The diffraction patterns obtained are shown in figure 2. All compounds exhibited a cubic structure and no impurity phases were detected within the limits of the method.

All samples exhibited the $L_1$ structure and the lattice parameters at 300 K were determined to $a = 5.733 \text{Å}$, $a = 5.819 \text{Å}$ and $a = 6.066 \text{Å}$ for Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn, respectively. These values were measured at room temperature using Mo-K$_\alpha$ radiation. They are summarized in table 1 and compared with calculated (structural optimization) values as well as values previously published by other authors. The values obtained are in good agreement with previously published values [26–28].

Further, the temperature dependence of the lattice parameter of the Ge- and Sn-based compounds was studied using synchrotron radiation. The results are displayed in figure 3. In both compounds, the lattice parameter exhibits a nonlinear dependence and decreases by about 0.25 per cent when the temperature is reduced from 300 to 20 K. The data were fitted to a $a(T) = a_0(1 + \alpha T + \beta T^2)$ model for the thermal expansion. For both compounds, the linear expansion coefficients are $\alpha \approx 5 \times 10^{-6} \text{K}^{-1}$ and the quadratic terms are of the order of $\beta \approx 10^{-8} \text{K}^{-2}$. The order of magnitude of both coefficients is typical for most metals.

EDX spectroscopy was performed on the compounds. The results of the quantitative chemical analysis are presented in table 2.
Figure 2. Powder XRD of the Co$_2$YZ compounds with $Z = \text{Si, Ge and Sn}$. The diffraction patterns are measured at room temperature with Mo-K$_\alpha$ radiation. (Online version in colour.)

Table 1. Lattice parameters of Co$_2$Ti$Z$ compounds with $Z = \text{Si, Ge and Sn}$. The experimentally determined lattice parameters $a_{\text{exp}}$ are compared with values from a structural optimization $a_{\text{calc}}$ and values from the literature $a_{\text{lit.}}$.

| compound     | $T$ [K] | $a_{\text{exp}}$ [Å] | $a_{\text{calc}}$ [Å] | $a_{\text{lit.}}$ [Å] |
|--------------|---------|-----------------------|------------------------|------------------------|
| Co$_2$TiSi   | 300     | 5.733                 | 5.758                  | 5.743 [26]             |
| Co$_2$TiGe   | 300     | 5.819                 | 5.850                  | 5.831 [27]             |
|              | 20      | 5.808                 |                        |                        |
| Co$_2$TiSn   | 300     | 6.066                 | 6.093                  | 6.076 [28]             |
|              | 20      | 6.053                 |                        |                        |

The EDX analysis of the cleaved sample surfaces revealed a homogeneous composition with only small deviations from the $2 : 1 : 1$ composition. On the edges of the samples, small Al impurities were found. The Al was introduced by the blade that was used for cutting. In figure 4, the SEM micrograph of the Co$_2$TiSi surface is displayed. Two segregations are identified at the surface. The first one, denoted by A at the cutting edges, is the aforementioned Al. It is found for all three compounds. The second segregation, denoted by B, is an accumulation of elementary Si. The Si impurity covers an area of about 4000 $\mu$m$^2$. The Ge- or Sn-containing compounds exhibit a uniform composition. Owing to the surface roughness, the error is approximately 2 per cent.
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Figure 3. Temperature dependence of the lattice parameter of (a) Co$_2$TiGe ($a_0 = 5.8069$ Å) and (b) Co$_2$TiSn ($a_0 = 6.0525$ Å). The photon energy was set to approximately 7111.96 eV. (Online version in colour.)

Table 2. Chemical composition of the Co$_2$Ti$Z$ compounds. Values are given in atomic %.

| element | Co$_2$TiSi | Co$_2$TiGe | Co$_2$TiSn |
|---------|------------|------------|------------|
| Co      | 49         | 50         | 53         |
| Ti      | 23         | 23         | 25         |
| Z       | 28         | 27         | 22         |

(b) Magnetic properties

The Co$_2$-based Heusler alloys that are half-metallic ferromagnets show a Slater–Pauling-like behaviour for the magnetization, which means that the saturation magnetization scales linearly with the number of valence electrons [21,29]. This results in a theoretical magnetic moment of 2$\mu_B$ per formula unit at $T = 0$ K for all three compounds. The saturation magnetization data measured at 5 K are shown in figure 5 and reveal that all three
compounds fulfil the Slater–Pauling rule and therefore are potential half-metallic ferromagnets. The magnetic moments at 5K are 1.96 $\mu_B$, 1.94 $\mu_B$ and 1.97 $\mu_B$ per formula unit for Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn, respectively. The Curie temperature $T_C$ was determined from the temperature dependence of the magnetization measured in an induction field of $\mu_0 H = 10 \text{ mT}$ (see inset of figure 5). The values for $T_C$ are 380 K for Co$_2$TiSi and Co$_2$TiGe and 355 K for Co$_2$TiSn. For Co$_2$TiSi a $T_C$ of 385 K was predicted by Chen et al. [30], which is in very good agreement with the experimentally obtained value here.

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X-ray absorption experiments were conducted at room temperature. Element-specific data were derived from the circular dichroism in X-ray absorption (XMCD). Spin and orbital moments that were calculated using the sum rules are summarized in Table 3. We have assumed \( N_h(\text{Co}) = 2.5 \) and \( N_h(\text{Ti}) = 8 \) for the number of 3d holes. We neglected the dipole term for the calculation of the spin moment. This contribution cancels out for polycrystalline samples. We also dispensed with the self-absorption correction because this correction is smaller than the statistical error for Heusler compounds. For \( \text{Co}_2\text{TiGe} \) and \( \text{Co}_2\text{TiSn} \), the sum rule analysis for Ti led to very large values and opposite sign of the orbital moments. In these two cases, we determined the magnetic moment of Ti by a comparison of XMCD peak heights with data from \( Z = \text{Si} \). The sum of the atomic moments \( \mu_{\text{XMCD}} \) agrees fairly well with the magnetization determined by SQUID magnetometry. Smaller values of \( \mu_{\text{XMCD}} \) in the case of \( Z = \text{Si} \) might be explained by a non-saturated magnetization owing to the limitation of the external field for the XMCD measurement. For all \( \text{Co}_2\text{TiZ} \) compounds, the magnetization is clearly dominated by the Co spin moment and a relatively large (for \( \text{Co}_2 \)-based Heusler compounds) contribution of the Co orbital moment (Table 3). A direct comparison of the Ti XMCD spectra with reference spectra clearly demonstrates the antiparallel alignment of the Ti magnetic moment. All three \( \text{CoTiZ} \) compounds are ferrimagnets [23]. Using the ratio of the SQUID data for 300 and 5K, we extrapolated the element-specific magnetic moments to low temperatures assuming a constant proportionality factor. The Co atom comprises, at low temperatures, a magnetic moment of \( \approx 1 \mu_B \) independent of \( Z \).

**Table 3.** Comparison of element-specific magnetic moments derived from sum rule analysis and SQUID magnetometry for \( \text{Co}_2\text{TiZ} \) (\( Z = \text{Si}, \text{Ge} \) and \( \text{Sn} \)) at \( T = 300 \text{K} \). The sum moment \( \mu_{\text{XMCD}} \) results from a weighted sum of the atomic moments. Values are given in \( \mu_B \) per atom for element-specific moments and \( \mu_B \) per formula unit for the magnetization. Low-temperature (5K) data from SQUID magnetometry were used to extrapolate element-specific data to 5K. For the number of unoccupied 3d states, we assumed the values \( N_h(\text{Co}) = 2.5 \) and \( N_h(\text{Ti}) = 8 \). The error bar for the XMCD-derived values does not include systematic errors owing to background subtraction, saturation correction and the error of \( N_h \).

| \( Z \)   | \( \mu_{\text{spin}} \) | \( \mu_{\text{orb}} \) | \( \mu_{\text{XMCD}} \) | \( \mu_{\text{SQUID}} \) |
|----------|----------------|----------------|----------------|----------------|
| \( \text{Si} \) | 0.36 ± 0.02 | -0.02 ± 0.02 | 0.94 ± 0.05 | -0.05 ± 0.05 |
| \( \mu_{\text{spin}} \) | 0.02 ± 0.02 | 0 ± 0.02 | 0.05 ± 0.05 | 0 ± 0.05 |
| \( \mu_{\text{orb}} \) | 0.75 ± 0.12 | 1.96 | 1.96 ± 0.10 |
| \( \mu_{\text{XMCD}} \) | 1.21 ± 0.10 | 1.96 ± 0.10 |
| \( \text{Ge} \) | 0.49 ± 0.02 | -0.03 ± 0.02 | 0.87 ± 0.05 | -0.05 ± 0.03 |
| \( \mu_{\text{spin}} \) | 0.07 ± 0.02 | 0 ± 0.02 | 0.12 ± 0.05 | 0 ± 0.05 |
| \( \mu_{\text{orb}} \) | 1.09 ± 0.12 | 1.94 | 1.94 ± 0.10 |
| \( \mu_{\text{XMCD}} \) | 1.22 ± 0.10 | 1.94 ± 0.10 |
| \( \text{Sn} \) | 0.56 ± 0.02 | -0.03 ± 0.02 | 0.93 ± 0.05 | -0.05 ± 0.03 |
| \( \mu_{\text{spin}} \) | 0.05 ± 0.02 | 0 ± 0.02 | 0.08 ± 0.05 | 0 ± 0.05 |
| \( \mu_{\text{orb}} \) | 1.19 ± 0.12 | 1.97 | 1.97 ± 0.10 |
| \( \mu_{\text{XMCD}} \) | 1.28 ± 0.10 | 1.97 ± 0.10 |
(c) Valence band photoemission spectroscopy

High-energy valence band photoemission spectroscopy was performed as an indication for the correctness of the band structure calculations. Figure 6 displays the valence band photoemission spectra and the calculated total density of states of the three compounds investigated here. For better comparison, the density of states is convoluted by a Fermi–Dirac distribution ($T=300$ K) and smoothed by Gaussian with a width of 250 meV. The latter accounts for the experimental resolution but neglects, however, any broadening caused by lifetime effects. The photoemission spectra were taken at room temperature using an excitation energy of approximately 6 keV. It was previously demonstrated that the cross sections of the contributing states ($s$, $p$ and $d$) are nearly equal at this photon energy [15,31]. This allows a direct comparison of the photoelectron spectra and the calculated density of states. The measured values agree well with the calculated ones and therefore are a good basis for the calculation of the transport properties, although one should keep in mind that the measurements are spin integrated and therefore only the comparison with the total density of states is viable.

(d) Transport properties

(i) Electrical resistivity

Figure 7a shows the temperature dependence of the resistivity $\rho$ for Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn. The resistivity behaviour is metallic for all compounds in the low-temperature range from 2 K to the respective Curie temperature. At $T_C$,
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magnetic field, $m_0H(T)$

current density, $J(T)\text{A/m}^2$

resistivity, $r(T)\text{(\mu\Omega m)}$

Fig. 7. Measured temperature-dependent electrical resistivity $\rho$ of Co$_2$TiZ compounds with $Z = \text{Si, Ge or Sn (a).}$ Magnetoresistance (MR) as a function of the applied magnetic field ($b$) for Co$_2$TiSn at $T = 306\text{K.}$. (a) Squares with solid line, Co$_2$TiSi; circles with solid line, Co$_2$TiGe; triangles with solid line, Co$_2$TiSn. (Online version in colour.)

a cusp-type transition is observed [32]. From there the resistivity declines to 550 K and stays nearly constant at higher temperatures. The Curie temperatures can be estimated from the maxima of the resistivities. The determined values are 370, 350 and 360 K for Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn, respectively. The values agree well with those obtained from the magnetic measurements. The measurements agree well with previous findings of other investigations for temperatures below 450 K [33]. Above $T_C$, a decrease in the resistivity is observed. The decrease is very pronounced up to about 600 K and stays nearly constant at higher temperatures. This behaviour leads to a significant anomaly in the resistivity at $T_C$. Other than in many ferromagnetic materials, here the Curie temperature can be easily related to the maximum of the resistivity.

Similar, cusp-type anomalies of the resistivity close to $T_C$ are very typical for the manganites, which show a large negative magnetoresistance (MR) around $T_C$ [34,35]. This was also observed in GdI$_2$, which shows a large room temperature MR of around 70 per cent at 7 T [36]. For intermetallic compounds, these anomalies were only observed for Heusler compounds [37,38]. In figure 7b, the MR of Co$_2$TiSn at $T = 306\text{K}$ is shown as defined by $[R(B) - R(0\text{Oe})]/R(0\text{Oe})$. In an applied magnetic field of $\mu_0H = 4\text{T}$, the MR exceeds 55 per cent, which is an enormous value for a polycrystalline sample at room temperature.

(ii) Seebeck coefficient

Figure 8 shows the Seebeck coefficient ($S$) that was measured for temperatures from 2 to 950 K. The values decrease with increasing temperature up to the Curie temperature and stay almost constant at higher temperatures. The mean values above $T_C$ are $-35, -31$ or $-51\text{\mu\Omega K}^{-1}$ for Co$_2$TiSi, Co$_2$TiGe and Co$_2$TiSn,
respectively. The maximum absolute values are rather large compared with most of the elemental metals and are close to the Seebeck coefficient of elemental Co, which exhibits approximately $-30$ to $-45 \mu V K^{-1}$ at temperatures between 300 and 500 K.

The Seebeck coefficient of all three investigated compounds is negative over the entire temperature range. For Co$_2$TiSn, a negative increase in the Seebeck coefficient is observed at approximately 80 K. This is close to $T/\Theta_D \approx 0.2$, where the largest influence of a phonon drag is expected and with $\Theta_D$ being the Debye temperature. This assumption is in agreement with the measurement of the thermal conductivity in which a peak at low temperatures is observed. The Seebeck coefficient provides a sensitive test of the electronic structure for metals in the vicinity of the Fermi energy. The rather large constant Seebeck coefficients above the Curie temperatures up to at least 950 K could be achieved by filling up the flat band in the $\Delta$ direction in the minority spin channel just above $e_F$ (figure 1c). The constant Seebeck coefficients above the Curie temperatures mean that the energy of the Fermi level is pinned in a wide temperature range in these compounds [13,39] and therefore the thermovoltages have a linear temperature dependence that makes these compounds suitable materials for future thermoelectric devices such as thermocouples. With an Al doping of the $Z$-position in the Co$_2$TiZ ($Z = \text{Si, Ge or Sn}$) compounds, one can tune their Curie temperature to lower values [40] and therefore tune the working temperature of thermocouples designed using these materials. In cubic systems, the Seebeck coefficient is derived from the scalar electrical resistivity $\rho$ and thermal conductivity $\nu$: $S = \rho \times \nu$. Therefore, the constant value of the Seebeck effect means that the product of $\rho$ and $\nu$ has to be constant, so they have to compensate each other’s dependency.
5. Summary and conclusion

In summary, the Co$_2$TiZ ($Z = $ Si, Ge or Sn) compounds were investigated theoretically and experimentally. Band structure calculations predict half-metallic ferromagnetism for all three compounds. The size of the minority band gap amounts to $\Delta E_{\text{HMF}} = 500$ meV and the Fermi energy is located close to the middle of the gap. The majority band structure is metallic with a single band crossing $e_F$ in the $\Delta$ direction. The Curie temperature and the magnetic moment were determined by SQUID measurements and reveal that all three compounds fulfill the requirement for half-metallicity according to the Slater–Pauling rule and have Curie temperatures well above room temperature. All compounds show a metallic-like resistivity for low temperatures up to their Curie temperature. From there on they change to semiconducting-like behaviour. This behaviour is attributed to a ferromagnetic to paramagnetic transition that strongly influences the band structure. The Seebeck coefficients are all negative and reach their maximum values at their respective Curie temperatures. The highest value achieved is $-52\,\mu\text{VK}^{-1}\text{m}^{-1}$ for Co$_2$TiSn. Furthermore, the Seebeck coefficients of all three compounds are rather large for metals and constant above the Curie temperatures. Therefore, the temperature dependence of the thermovoltages is linear, which ensures a stable conversion efficiency even at high temperatures. This makes the compounds very attractive as materials for thermocouples or thermoelectric generators. The combination of half-metallicity and the constant large Seebeck coefficient over a wide temperature range makes these compounds interesting materials for further spinocaloric and thermoelectric investigations.

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