Quantum mechanically guided design of Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ ($X$=B, Si, P, S) metallic glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 J. Phys.: Condens. Matter 24 175402

(http://iopscience.iop.org/0953-8984/24/17/175402)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 131.169.38.143
The article was downloaded on 30/04/2012 at 13:24

Please note that terms and conditions apply.
Quantum mechanically guided design of Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ ($X = B, Si, P, S$) metallic glasses

C Hostert$^1$, D Music$^1$, J Bednarcik$^2$, J Keckes$^3$ and J M Schneider$^1$

$^1$ Materials Chemistry, RWTH Aachen University, D-52056 Aachen, Germany
$^2$ Deutsches Elektronen Synchrotron DESY, D-22607 Hamburg, Germany
$^3$ Department of Materials Physics, Montanuniversität Leoben and Erich Schmid Institute for Materials Science Austrian Academy of Sciences, A-8700 Leoben, Austria

E-mail: hostert@mch.rwth-aachen.de

Received 7 February 2012, in final form 12 March 2012
Published 3 April 2012
Online at stacks.iop.org/JPhysCM/24/175402

Abstract

A systematic ab initio molecular dynamics study was carried out to identify valence electron concentration and size induced changes on structure, elastic and magnetic properties for Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ ($X = B, Si, P, S$). Short range order, charge transfer and the bonding nature are analyzed by means of density of states, Bader decomposition and pair distribution function analysis. A clear trend of a decrease in density and bulk modulus as well as a weaker cohesion was observed as the valence electron concentration is increased by replacing B with Si and further with P and S. These changes may be understood based on increased interatomic distances, variations in coordination numbers and the electronic structure changes; as the valence electron concentration of X is increased the X bonding becomes more ionic, which disrupts the overall metallic interactions, leading to lower cohesion and stiffness. The highest magnetic moments for the transition metals are identified for $X = S$, despite the fact that the presence of X generally reduces the magnetic moment of Co. Furthermore, this study reveals an extended diagonal relationship between B and P within these amorphous alloys. Based on quantum mechanical data we identify composition induced changes in short range order, charge transfer and bonding nature and link them to density, elasticity and magnetism. The interplay between transition metal d band filling and s–d hybridization was identified to be a key materials design criterion.

1. Introduction

Computational design based on quantum mechanics has been employed within the past few decades to promote innovations. Due to inherent benefits of this theoretical methodology, such as low costs in comparison to extensive experimental research and the available correlation between properties and electronic structure, research efforts have aimed to develop approaches allowing for property prediction. First principles methods often enable a deeper understanding of the immanent physical mechanisms defining certain material attributes. As a result, material properties can be designed and tailored by employing ab initio methods: the impact of element substitutions was studied for arthropod exoskeletons [1], semiconductor spintronics [2], hard coatings [3, 4], MAX phases [5, 6], lithium battery electrolytes [7] or thermoelectrics [8], to name a few. The properties investigated cover a wide range from elastic [1, 4] over electronic properties [9, 10, 2] and bonding nature [7, 2] to magnetic properties [2, 11] as well as phase stability [9, 8, 5, 3, 6]. While the bulk of the work is carried out for crystalline materials, quantum mechanical descriptions of the glassy state are scarce. However, metallic glasses have been investigated regarding the effect of (optimized) composition...
on atomic structure and glass-forming ability [12–17]. Other fields of interest for computationally based research on metallic glasses are composition dependent dynamic properties [17] or the effect of valence electron concentration on the glass transition temperature [18]. Our previous work on Co–Fe–Ta–B metallic glass [19] and its elastic and magnetic properties was one of the first a priori based investigations for Co-based glasses [20]. A few on associated systems based on magnetic elements such as Fe [21–24] have been published. Systematic ab initio studies on the effect of element substitution are rare, e.g. the work done by He et al [25] and have not been reported for Co-based glasses.

Within the family of Co-based metallic glasses, the metalloid elements, chiefly B and Si, are reported to play an important role for a stable supercooled liquid region [26–31], high strength [30] and magnetic properties [27, 29, 30]. The impact of the metalloid element in particular seems to be wide ranging but has not yet been studied systematically, although an increase in valence electron concentration, size or electronegativity of the metalloid element is expected to impact the overall properties. Namely, it is reported that a high average difference in electronegativity among the elements leads to a high glass-forming ability [32]. While an investigation on the impact of Si substitution of B in Co–Fe–Ta–B was reported [33], P and/or S substitutions of B have not yet been considered experimentally, although P is reported to increase the critical thickness (if substituted for 2 at.% B) and the glass-forming ability within the Fe-based systems Fe28Si15B11 [34] and Fe58.3Cr6.0Si2.5B7.5P8.8Cr2.2Mo2.5Al2.1 [35].

Co–Fe–Ta–B metallic glasses [19] were modeled using an ab initio molecular dynamics approach which was validated regarding short range order, density and elastic properties by comparison with experimental data. Within this study, we investigate, based on a previously validated computational procedure [19], the effect of valence electron concentration (VEC) and size of the X element in Co31Fe20Ta5.5X31.5 (X = B, Si, P, S) on the metallic glass properties and seek to contribute towards a better understanding of composition induced changes in properties.

2. Theoretical methods

Our theoretical studies are executed employing two ab initio codes, namely the codes OpenMX [36] and the Vienna ab initio simulation package (VASP) [37]. OpenMX is based on density functional theory (DFT) [38] and employed to perform ab initio molecular dynamics simulations. The generalized gradient approximation and a linear combination of pseudoatomic orbitals [39, 40] were used. Based on the known model system Co31Fe20Ta5.5B31.5 [19], B was systematically replaced by Si, P and S. In each initial configuration the atoms were placed on ad hoc random positions in a bcc supercell. All cells contained 10% randomly introduced vacancies independent of atomic species (115 atoms in total). This type of cell is identical to the cells used in our earlier studies [19]. As basis functions Co5.5 s2p1d1, Fe5.0 s1p2d1, Ta7.0 s2p1d1f1, B4.5 s2p2, Si5.0 s2p1, P6.0 s2p1d1 and S6.0 s2p2d1 were used. The first symbol and number designate the chemical name and confinement radius, respectively, followed by the description of orbitals used. All four systems were held at a temperature of 4000 K for 400 fs by scaling the velocities and were then quenched to 0 K, simulating an infinite cooling rate. At 0 K all configurations were relaxed in terms of atomic positions and volumes. The force convergence criterion was set to 0.51 eV Å−1.

All static calculations, including the extraction of total and partial DOS as well as bonding analysis were conducted employing the second code, VASP, which is also DFT based [38]. The applied parameters for the VASP calculations were as follows: the generalized gradient approximation (Perdew–Wang 91) exchange–correlation functional [40] with Vosko–Wilk–Nusair [41] spin interpolation, based on ultrasoft pseudopotentials [39]. A Brillouin zone on a 3 × 3 × 3 Monkhorst–Pack grid [42], centered at the Γ-point, as well as an energy cutoff of 500 eV were applied. Furthermore an electron smearing of 0.2 eV based on the tetrahedron method with Blöchl corrections [43, 44] and a convergence criterion of 0.01 meV for the total energy was set. All calculations were carried out at 0 K. Cohesive energies are defined as negative values. The bulk moduli were obtained by the uniform compression approach and fitting the energy–volume curves to the Birch–Murnaghan equation of states [45]. The effective charge of an element is defined within this study as the charge difference of a neutral atom in comparison to the present charge state within the alloy [46]. The charge was deduced by the Bader charge analysis [47] as implemented in the program written by Henkelman and co-workers [48, 49] by dividing the electron density distribution along surfaces, implying a gradient of zero along the surface normal. Convergence was tested by calculating the charge with a series of variable grids.

3. Results and discussion

Bonding nature and internal atomic arrangements, elastic as well as magnetic properties were analyzed in terms of density of states, effective charge, pair distribution functions as well as bulk modulus and transition metal magnetic moments. All characteristics are studied as a function of X and hence of valence electron concentration and atomic size within Co43Fe20Ta5.5X31.5 (X = B, Si, P, S).

We start with the analysis of the electronic structure. In figure 1 partial DOS are plotted for all alloys studied. Only the orbitals exhibiting the highest population are taken into account: 3d for Co and Fe, 5d for Ta and 3s/3p for B/Si/P/S.

The metallic character is present in all four systems probed; the occupied states around the Fermi level are consistent with a metallic bonding. Previously, strong interactions between Co and B as well as Fe and B were reported [19]. Here, in analogy, strong interactions between Co and X as well as Fe and X (X = Si, P, S) can be identified contributing towards the overall (inter-) metallic character of Co43Fe20Ta5.5Si31.5, Co43Fe20Ta5.5P31.5 and Co43Fe20Ta5.5S31.5. Co and X as well as Fe and X atoms form clusters interconnected via metallic bonds. We already reported Co–B as well as Fe–B to be the strongest hybridized
Figure 1. Partial density of states for Co$_{43}$Fe$_{20}$Ta$_5$X$_{31.5}$ ($X = B, Si, P, S$) investigated in this study and [19]. Co d states are displayed as bold solid, Fe d as bright solid, X p and X s states as dark solid and Ta d states as dotted lines. The Fermi level is set to 0 eV. Up and down states of Co and Fe are provided as positive and negative values, respectively.

Figure 2. Effective charge of Co (squares), Fe (circles), Ta (upward facing triangles), B, Si, P and S (downward facing triangles) as a function of ionic potential of the X element for all probed configurations Co$_{43}$Fe$_{20}$Ta$_5$X$_{31.5}$ ($X = B, Si, P, S$), which is now shown to be valid for $X = Si, P$ and S too. The strongest hybridization within (Co, Fe)–X ($X = B, Si, P, S$) is identified to be Co–S, followed by Co–B, Fe–P and Fe–Si. The states of cobalt and iron are spin polarized for all configurations probed. A replacement of B by Si in particular, introduces a strong magnetic polarization, observable as intense peaks in the up and down states (see figure 1).

To evaluate ionic contributions, which may be significant for explaining elastic properties, the Bader charge analysis is employed to study the changes in the effective charge induced by valence electron concentration variation. Figure 2 shows the effective charge as a function of ionic potential of each atomic species for all four configurations probed.

The ionic potential is defined as $\Phi = Z/r$ (where $Z$ is the effective charge of the ion and $r$ is the ionic radius). This ratio is a measure of charge density and ionic interaction. A variation in the ionic potential of $X$ in the range of 0.1–0.21 C pm$^{-1}$ does not affect the most populated species, Co and Fe to a larger extent. These elements are mainly metallic in nature while the third metal, Ta, is most depleted irrespective of $X$. The effective charge of the $X$ element, being the second most abundant constituent, is negative in the case of $X = B, P$ and S. It can be seen that an increase in ionic potential when $X$ is systematically varied from Si to B, P and further to S, shifts the general metallic bond character of the simulated metallic glasses towards a more ionic bonding. If B is substituted by Si, resulting in a decrease of the ionic potential for $X$, fewest effective charges for all constituents can be stated. A further $X$ substitution from Si to P increases the ionic potential of $X$ from 0.1 to 0.13 C pm$^{-1}$ and drastic charge transfer from mainly tantalum to the $X$ element is realized. Co$_{43}$Fe$_{20}$Ta$_5$P$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_5$B$_{31.5}$ are
similar in the effective charges of all four constituents. The maximum difference is found to be 0.096 \text{ C pm}^{-1} for Ta in both configurations. A high charge transfer can be further adduced for the X substitution, resulting in the \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{B}_{24,5} \text{ configuration}. The effective charge of S varies with respect to B by 0.43 \text{ C pm}^{-1}. Sulfur as the element exhibiting the highest ionic potential and known for a high electronegativity is expected to form the most ionic bonds for all X elements probed. Hence it can be concluded that a large ionic potential of X results in a strong ionic interaction, which in turn is expected to decrease the stiffness of the amorphous alloys studied.

Pair distribution functions (PDFs) reveal short range order and were successfully employed for the validation of the \textit{ab initio} model used here [19]. We use PDFs to gain insight into the X induced changes on short range order by identification of atomic pair interactions. Figure 3 shows the comparison of two PDFs.

The first PDF (solid line) is obtained from \textit{ab initio} calculations with the VASP code by Fourier transformation of the calculated structure factor, without considering scattering lengths of the corresponding elements [37]. The second PDF shown in figure 3 (line + circles) is obtained based on a calculation in real space, taking type and position of each atom within the supercell into account [19]. Scattering lengths of the corresponding atomic types are included in this calculation. As one can see, the curve is shifted and the first pre-peak, visible in the \textit{ab initio} data, vanishes when scattering lengths are included into the PDF calculation. This can be understood by considering the low scattering power of B, which is not considered in the VASP code as all scattering lengths are equal to one [37]. Good agreement is obtained for the x-ray diffraction data with the calculated PDF including the scattering lengths [19]. The fact that the inclusion of scattering lengths has such a prominent effect on the PDF is due to the different mass and size and hence scattering power values of the atoms forming this alloy. Nevertheless, we will use \textit{ab initio} data directly obtained from the VASP code for the structural analysis and discussion on an atomic level of all four systems investigated, as provided in figure 4, to enable the comparison with other computational studies. It is apparent that all configurations studied exhibit no long range order.

The first coordination shell of \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{B}_{24,5} is of bimodal shape, centered at \sim 2 and 2.5 \text{ Å}, and is dominantly composed of (Co, Fe)–B and (Co, Fe)–(Co, Fe), (Co, Fe)–Ta and Ta–Ta interactions [19]. The small pre-peak located at 1.73 \text{ Å} may be assigned to B–B atomic pair correlations [19]. A more detailed analysis on the PDF of the related \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{B}_{24,5} glassy alloy can be found in our earlier work [19]. For the Si containing metallic glass \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{Si}_{31,5}, the distribution is unimodal and centered around 2.6 \text{ Å}, but it can still be subdivided into several contributions. The atomic pairs responsible for the shape of this peak are (Co, Fe, Ta)–Si, Fe–Co and Si–Si. A detailed peak analysis can be found in table 1.

As the valence electron concentration is increased by substituting Si with P, the pair distribution function for \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{P}_{31,5} shows a small pre-peak located below \sim 2 \text{ Å} and a pronounced second peak of bimodal shape. As listed in table 1, P–P pairs contribute to the pre-peak, which is in agreement with [51], while the first feature of the second peak is composed of P–P and Co–P interactions. Hence the P containing quaternary metallic glass is revealing similarities for the dominating atomic pairs at a certain distance to \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{B}_{31,5}. As the valence electron concentration is increased by substituting P with S, the PDF for \text{Co}_{43,5}\text{Fe}_{20}\text{Ta}_{5,5}\text{S}_{31,5} shows a rather broad first peak around 2.5 \text{ Å}. The first three vertices can be attributed to Co–S, Fe–S and a mixture of Ta–S, Fe–Fe–, Co–Co and Co–Fe

Figure 3. Pair distribution function of Co_{43.5}Fe_{20}Ta_{5.5}B_{24.5}. \textit{ab initio} data from VASP (solid) and calculated with scattering lengths (line + circles).

Figure 4. Pair distribution functions of Co_{43.5}Fe_{20}Ta_{5.5}X_{31.5}, X = B, Si, P and S.
interactions as listed in table 1. The shoulder to the right arises from Co–Ta and Co–Co atomic pairs. It is worth mentioning that for Co$_{43}$Fe$_{20}$Ta$_{5.5}$S$_{31.5}$ no S–S interaction could be identified. While Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$P$_{31.5}$ show similarities in the shape of PDFs and hence in nearest neighbors, which account for short range order, the same can be stated for Co$_{33}$Fe$_{20}$Ta$_{5.5}$Si$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$S$_{31.5}$. Atomic pairs which possess strong bonds according to DOS analysis reveal indications for interactions in the PDFs as well. Namely, (Co, Fe)–X (X = Be, Si, P, S) are identified to form strong and short bonds based on both DOS and PDF data.

The extracted coordination numbers ($N_{ij}$) for the Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ metallic glass simulated in this study agree well with the values reported by Kaban et al. [50] (see table 1). Maximum deviations are observed for Ta containing correlations, which may be due to the limited number of Ta atoms present in the supercell, causing poor statistics. B–B pairs are found to be present in our model, which is consistent with the data reported by Kaban et al. [50].

We extracted $N_{BB}$ to be 1.1, which is in agreement with Pusztai and Sváb [52], where $N_{BB}$ ≈ 1 was obtained from reverse Monte Carlo simulations of Ni$_6$B$_{15}$. Short boron chains have formed in the B containing system (see figure 5). Here B atoms are displayed as black spheres, surrounded by their electron density isosurfaces, indicated as halos. Interconnected isosurfaces suggest chemical bonding between the respective atoms. The formation of B chains observed here is in agreement with [52] and [53], while no evidence for the formation of a B network as suggested by Kaban et al for $N_{BB}$ = 2.3 [50] could be identified. As the valence electron concentration is increased by substituting B with Si, an increase in coordination number can be observed for (Co, Fe, Ta, X)–X and X–(Co, Fe) (X = B, Si) pairs as listed in table 1. The aspect of an increased coordination number for X = Si is further supported by a total coordination number analysis for X in all four configurations under study: ($N_{X}$) = 8.2/12.0/8.9/7.1 for X = B/Si/P/S, respectively and it is hence obviously higher for the Si containing glass. The total coordination number of 12.0 for Si is large compared to ($N_{B}$), ($N_{P}$) and ($N_{S}$) and furthermore is in the same range as ($N_{Co}$) and ($N_{Fe}$). The already discussed similarity for the B and P containing metallic glasses as well as for Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ (X = Si, S) in terms of short range ordering is also observed within the coordination number data obtained from the PDF data (see table 1).

The similarities in effective charges of all four constituents, PDF shape, nearest neighbors and coordination number data between Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$P$_{31.5}$ as discussed above may be caused by the similar ionic potential (ratio between ionic radius and ionic charge). This phenomenon, known as the so-called ‘diagonal relationship’ [55–58] mainly occurring between elements of the second and third period, states that diagonally neighboring elements show similar chemical behavior. For instance, Be is more similar to Al than to B. Here, the addition of one valence electron is compensated by the larger ionic radius of Al. Hence, the ionic potentials of Be and Al are similar, resulting in similar properties [55, 56]. Although B and P are not directly adjacent, the ionic potentials for B and P are as close as for B and Si (see table 2). This fact, in combination with the high impact of atomic radii and effective charge on the here investigated properties, may explain the similarity between both metallic glasses Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$P$_{31.5}$. This is here referred to as an ‘extended diagonal relationship’.

After discussing the chemical bonding of the quaternary amorphous alloys, we proceed with the analysis of density as

---

**Table 1.** Mean nearest neighbor distances $d_{ij}$, their standard deviations $\sigma (d)$ and coordination numbers $N_{ij}/N_{ji}$ for Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ metallic glasses calculated in this study, [19] and [50].

<table>
<thead>
<tr>
<th>Pairs i,j</th>
<th>$d_{ij}$ (Å)</th>
<th>$\sigma (d)$ (Å)</th>
<th>$N_{ij}/N_{ji}$</th>
<th>Reference [50]</th>
<th>$d_{ij}$ (Å)</th>
<th>$\sigma (d)$ (Å)</th>
<th>$N_{ij}/N_{ji}$</th>
<th>$d_{ij}$ (Å)</th>
<th>$\sigma (d)$ (Å)</th>
<th>$N_{ij}/N_{ji}$</th>
<th>$d_{ij}$ (Å)</th>
<th>$\sigma (d)$ (Å)</th>
<th>$N_{ij}/N_{ji}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>X–X</td>
<td>1.84</td>
<td>0.08</td>
<td>1.1</td>
<td>2.3</td>
<td>2.60</td>
<td>0.17</td>
<td>2.9</td>
<td>2.08</td>
<td>0.31</td>
<td>1.6</td>
<td>2.27</td>
<td>0.13</td>
<td>2.6/1.7</td>
</tr>
<tr>
<td>Fe–X/X–Fe</td>
<td>2.17</td>
<td>0.11</td>
<td>2.9/1.9</td>
<td>2.3/1.5</td>
<td>2.45</td>
<td>0.10</td>
<td>3.6/2.4</td>
<td>2.25</td>
<td>0.20</td>
<td>2.6/1.7</td>
<td>2.23</td>
<td>0.10</td>
<td>3.2/4.6</td>
</tr>
<tr>
<td>Co–X/X–Co</td>
<td>2.01</td>
<td>0.05</td>
<td>3.1/4.4</td>
<td>3.7/5.1</td>
<td>2.33</td>
<td>0.08</td>
<td>4.0/5.8</td>
<td>2.05</td>
<td>0.18</td>
<td>3.4/4.8</td>
<td>2.23</td>
<td>0.10</td>
<td>3.2/4.6</td>
</tr>
<tr>
<td>Ta–X/X–Ta</td>
<td>2.53</td>
<td>0.14</td>
<td>4.1/0.8</td>
<td>2.9/0.5</td>
<td>2.78</td>
<td>0.22</td>
<td>4.6/0.9</td>
<td>2.29</td>
<td>0.20</td>
<td>4.0/0.8</td>
<td>2.59</td>
<td>0.15</td>
<td>4.1/0.8</td>
</tr>
<tr>
<td>Fe–Fe</td>
<td>2.50</td>
<td>0.10</td>
<td>2.8</td>
<td>4.6</td>
<td>2.51</td>
<td>0.22</td>
<td>2.8</td>
<td>2.46</td>
<td>0.14</td>
<td>3.0</td>
<td>2.51</td>
<td>0.21</td>
<td>1.9</td>
</tr>
<tr>
<td>Fe–Co/Co–Fe</td>
<td>2.39</td>
<td>0.12</td>
<td>6.0/2.8</td>
<td>5.6/2.6</td>
<td>2.41</td>
<td>0.17</td>
<td>5.0/2.3</td>
<td>2.41</td>
<td>0.14</td>
<td>6.1/2.8</td>
<td>2.48</td>
<td>0.23</td>
<td>4.8/2.3</td>
</tr>
<tr>
<td>Fe–Ta/Ta–Fe</td>
<td>2.71</td>
<td>0.16</td>
<td>0.9/2.7</td>
<td>1.1/4.0</td>
<td>2.63</td>
<td>0.17</td>
<td>0.8/2.6</td>
<td>2.55</td>
<td>0.17</td>
<td>0.8/2.6</td>
<td>2.77</td>
<td>0.24</td>
<td>0.8/2.4</td>
</tr>
<tr>
<td>Co–Co</td>
<td>2.41</td>
<td>0.07</td>
<td>5.5</td>
<td>7.0</td>
<td>2.46</td>
<td>0.11</td>
<td>4.6</td>
<td>2.41</td>
<td>0.10</td>
<td>5.1</td>
<td>2.47</td>
<td>0.14</td>
<td>4.2</td>
</tr>
<tr>
<td>Co–Ta/Ta–Co</td>
<td>2.63</td>
<td>0.23</td>
<td>1.1/7.4</td>
<td>1.0/8.1</td>
<td>2.66</td>
<td>0.24</td>
<td>0.9/6.1</td>
<td>2.52</td>
<td>0.23</td>
<td>0.8/5.6</td>
<td>2.69</td>
<td>0.25</td>
<td>0.7/4.7</td>
</tr>
</tbody>
</table>

---

**Figure 5.** Isosurfaces of electron density for Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ (equi-density level of 0.095 (au)). Solely B atoms are displayed for clarity using the VESTA software [54].
This is consistent with other amorphous systems, such as energy is accompanied by an increase in bulk modulus. It is varied from B to Si and S, a decreasing trend in cohesive energy is shown in figure 6. We correlate bulk moduli with density and cohesive energy, as given in table 2. The densities extracted from the theoretical models decrease steadily when B is substituted by Si, P and S. For Co,Ta,B a density of 8.19 g cm^{-3} can be reported, the S containing glass gives a density of 7.15 g cm^{-3}, which implies a reduction of 12.7%. The covalent radii of Si, P and S increase by 35%, 29% and 24% as compared to the B radius. Although there is a decreasing trend in radius gain when the X element is substituted by Si, P and further by S, the density of each metallic glass is decreasing. This may be understood by an increase in average atomic distances increase by 11%. The increase in atomic distances increase by 11%. The increase in atomic bond length and/or the formation of cavities. An increase of bond length may be causative for the density decrease in Co,Ta,B and Co,Ta,P compared to Co,Ta,B. Our analysis shows that the averaged and weighted distances increase by 2.4% and 5.5%, respectively (all pairs with Ta atoms were neglected, due to the limited number of atoms, as already discussed above). A corresponding decrease of 7% and 13% in density correlates well with the changes in distances since they result in a density decrease of 7% and 17%. For Co,Ta,P it may be speculated that cavities cause a slight decrease in density of 1.5% (compared to the B containing glass), although the net atomic distances increase by 11%. The increase in atomic radius of Si by 35% as compared to B and higher coordination numbers for (Co, Fe, Ta, Si)–Si and Si–(Co, Fe) pairs may support this speculation. A correlation of coordination and the presence of cavities is reported in [60] as well, where cavities are linked with the packing of quasi-equivalent clusters. By also taking the results of coordination analysis into account, one may thus postulate a non-uniform packaging of clusters and cavities for the Si containing amorphous alloy.

The bulk moduli, provided in table 2, decrease when X is varied within Co,Ta,B and Co,Ta,P compared to Co,Ta,B. Our analysis shows that the averaged and weighted distances increase by 2.4% and 5.5%, respectively (all pairs with Ta atoms were neglected, due to the limited number of atoms, as already discussed above). A corresponding decrease of 7% and 13% in density correlates well with the changes in distances since they result in a density decrease of 7% and 17%. For Co,Ta,P it may be speculated that cavities cause a slight decrease in density of 1.5% (compared to the B containing glass), although the net atomic distances increase by 11%. The increase in atomic radius of Si by 35% as compared to B and higher coordination numbers for (Co, Fe, Ta, Si)–Si and Si–(Co, Fe) pairs may support this speculation. A correlation of coordination and the presence of cavities is reported in [60] as well, where cavities are linked with the packing of quasi-equivalent clusters. By also taking the results of coordination analysis into account, one may thus postulate a non-uniform packaging of clusters and cavities for the Si containing amorphous alloy.

The bulk moduli, provided in table 2, decrease when X is varied within Co,Ta,B and Co,Ta,P compared to Co,Ta,B. Our analysis shows that the averaged and weighted distances increase by 2.4% and 5.5%, respectively (all pairs with Ta atoms were neglected, due to the limited number of atoms, as already discussed above). A corresponding decrease of 7% and 13% in density correlates well with the changes in distances since they result in a density decrease of 7% and 17%. For Co,Ta,P it may be speculated that cavities cause a slight decrease in density of 1.5% (compared to the B containing glass), although the net atomic distances increase by 11%. The increase in atomic radius of Si by 35% as compared to B and higher coordination numbers for (Co, Fe, Ta, Si)–Si and Si–(Co, Fe) pairs may support this speculation. A correlation of coordination and the presence of cavities is reported in [60] as well, where cavities are linked with the packing of quasi-equivalent clusters. By also taking the results of coordination analysis into account, one may thus postulate a non-uniform packaging of clusters and cavities for the Si containing amorphous alloy.

Table 2. Theoretical results of the quaternary systems investigated in this study and [19], as well as the number of electrons, ionic radii and ionic potentials of B, Si, P and S, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Co–Fe–Ta–B</th>
<th>Co–Fe–Ta–Si</th>
<th>Co–Fe–Ta–P</th>
<th>Co–Fe–Ta–S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohesive energy/atom (eV)</td>
<td>−7.4552</td>
<td>−7.1529</td>
<td>−7.4592</td>
<td>−6.6234</td>
</tr>
<tr>
<td>B (GPa)</td>
<td>209^a</td>
<td>168</td>
<td>161</td>
<td>118</td>
</tr>
<tr>
<td>ρ (g cm^{-3})</td>
<td>8.19^b</td>
<td>8.07</td>
<td>7.62</td>
<td>7.15</td>
</tr>
<tr>
<td>Cell volume (Å^3)</td>
<td>1157</td>
<td>1395</td>
<td>1435</td>
<td>1537</td>
</tr>
<tr>
<td>Valence electrons</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Ionic radius (pm)</td>
<td>27^b</td>
<td>40^b</td>
<td>38^b</td>
<td>29^b</td>
</tr>
<tr>
<td>Ionic potential (C pm^{-1})</td>
<td>0.11</td>
<td>0.10</td>
<td>0.13</td>
<td>0.21</td>
</tr>
</tbody>
</table>

^a From reference [19].  
^b Ionic radii ([59]), for X = B, Si, P and S.

Figure 6 shows the normalized magnetic moments of Fe and Co within all four metallic glasses under study with respect to the magnetic moments of pure (bcc) Fe and (hcp) Co, respectively. The magnetic moment of Fe in these quaternary glasses is also consistent with the VEC induced increase in ionic bond character (see figure 2). The deviant behavior for X = P may stem from the size differences. For instance, it is known that the cohesive energies of small diamond and large Nb are −7.37 and −7.57 eV, while their bulk moduli are 443 and 170 GPa [64]. More work is needed to analyze the anomaly for X = P.

Figure 7 shows the normalized magnetic moments of Fe and Co within all four metallic glasses under study with respect to the magnetic moments of pure (bcc) Fe and (hcp) Co, respectively.
observed for Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$. Within the alloys studied here, a maximum deviation in magnetic moments of 34% is identified for Co$_{43}$Fe$_{20}$Ta$_{5.5}$S$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$P$_{31.5}$, while Co$_{43}$Fe$_{20}$Ta$_{5.5}$S$_{31.5}$ is still 33% lower than the reference magnetic moment for pure cobalt. The observation that the magnetic moment of Co is reduced may be explained by the fact that metalloid elements seem to reduce the magnetic moments of the transition metals within amorphous metallic alloys [65]. Ferromagnetism occurs due to unpaired d electrons, so we will discuss the magnetic moment values on the basis of the electronic structure. The DOSs extracted from our ab initio simulations agree well with the approach of Alben [66] that sp metalloid electrons hybridize with s/p/d electrons of the transition metals and form covalent bonds below the Fermi level as well as antibonding interactions above. When electrons move from these antibonding sites to the d-bands of Co, the magnetic moment will be reduced due to lowering of unpaired states, despite the fact that hardly any charge transfer is realized. Detailed analysis of the effective charge transfer, as well as an integration of the d-bands of Co, support this notion, indicating no drastic variation in charge for Co and less filled Co states for Co$_{43}$Fe$_{20}$Ta$_{5.5}$S$_{31.5}$ and hence the lowest reduction of the magnetic moment for Co within Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ (X = B, Si, P, S) metallic glasses. Furthermore, this fact corroborates the reduction of bulk modulus when X is varied from B to Si, P and S: the interaction between X and the transition metal becomes less strong due to less electron transfer from X to the d-bands of Co and Fe and hence a weaker s–d hybridization [67, 30]. The interplay between transition metal d band filling and s–d hybridization seems to be a key design criterion for high strength and soft magnetic metallic glasses.

4. Conclusions

We have carried out a systematic ab initio study of the quaternary Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ metallic glass system with X = B, Si, P, S. The composition induced changes on short range order, charge transfer and bonding nature were studied and correlated with density, elasticity and magnetism. Density of states as well as pair distribution functions indicate (Co, Fe)–X atomic pairs to be the shortest and strongest constituents. Bader charge analysis reveals a trend towards a more ionic bond character as B is substituted by P and S. Coordination numbers extracted for Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ are consistent with the literature [50, 52]. Density, bond length and coordination number analysis of the amorphous alloy Co$_{43}$Fe$_{20}$Ta$_{5.5}$Si$_{31.5}$ suggests a non-uniform distribution of clusters and cavities, exhibiting a different structural appearance than for the other systems studied. For Co$_{43}$Fe$_{20}$Ta$_{5.5}$X$_{31.5}$ (X = P, S) the increase in atomic distances is accompanied by a proportional decrease in density with respect to Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$. The bulk moduli of all amorphous alloys show a decreasing trend from 209 to 118 GPa when X is varied from B to Si, P and further to S. This can be understood by analyzing density and cohesive energy; a decrease in bulk modulus is attended by a decrease in density and caused by a weaker cohesion (less negative cohesive energy). Cohesion seems to be influenced by several factors such as the hybridization strength of the main constituents, the ionic potentials and the spatial distribution of atoms; a higher hybridization strength between Co and X seems to give rise to a stronger cohesion. Furthermore, a large ionic potential as well as a non-uniform distribution of clusters and cavities seem to reduce cohesion. Similarities between Co$_{43}$Fe$_{20}$Ta$_{5.5}$B$_{31.5}$ and Co$_{43}$Fe$_{20}$Ta$_{5.5}$P$_{31.5}$ may be due to an extended diagonal relationship between B and P caused by similar ionic potentials. The reduction of transition metal magnetic moments, especially for Co, may be attributed to the presence of the X element, giving rise to filled d states of Co and hence reduced magnetic moments. This effect is the least pronounced for X = S. Quantum mechanics enables the identification of composition induced changes on short range order, charge transfer and on the bonding nature and links them to density, elasticity and magnetism. The interplay between transition metal d band filling and s–d hybridization was identified to be a key materials design criterion.

Acknowledgments

The authors would like to acknowledge Deutsche Forschungsgemeinschaft (DFG) within the Collaborative Research Center (SFB) 761 ‘Steel—ab initio’. Financial support from the Zhejiang University—Helmholtz Research Collaboration Program is also gratefully acknowledged.

References

[1] Nikolov S, Fabritius H, Petrov M, Friák M, Lymerakis L, Sachs C, Raabe D and Neugebauer J 2010 Robustness and optimal use of design principles of arthropod exoskeletons...


[15] Huaaijun S, Qikui M, Yaqian D, Baolong S, Kimura H, Makino A and Inoue A 2010 Effects of B and Si contents on glass-forming ability and soft magnetic properties in (Co0.8Fe0.05)100–x(B0.8Si1.2)18 glassy alloys J. Appl. Phys. 107 09A319


[24] OpenMX version 3.5 was used in this study and is available at www.openmx-square.org


[55] Cartledge G H 1928 Studies on the periodic system. II. The ionic potential and related properties I J. Am. Chem. Soc. 50 2863–72
[58] Zdetsis A D 2011 Designing novel Sn–Bi, Si–C and Ge–C nanostructures, using simple theoretical chemical similarities Nanoscale Res. Lett. 6 362