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First-principles simulation of the elastic properties of multicomponent amorphous steels

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The local atomic structure and elastic properties of two series of multicomponent amorphous steels—with and without phosphorus addition—have been investigated by *ab initio* molecular dynamics. A comparison of neutron pair-distribution functions allowed the difference in local atomic organization for these two series to be explained in terms of the atomic size effect. The conclusions drawn on the basis of "empirical" consideration were confirmed by the results of first-principles simulations. The structural models obtained in the course of *ab initio* molecular-dynamics calculations were used for the simulation of the elastic properties and the results of the modeling revealed a close agreement with the experiment. This allowed us to elucidate a role of particular chemical elements in improving the ductility of particular compositions.

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I. INTRODUCTION

Bulk metallic glasses (BMGs) are promising from the application point of view. In comparison with regular crystalline alloys, they frequently demonstrate enhanced physical properties such as high mechanical strength, resistance to corrosion[1–3] and, in some cases (Fe-, Ni-, and Co-based metallic glasses), soft magnetic properties.[4–6] Bulk MG synthesis procedures have been well established. As a result, different families of BMG systems, such as those based on Zr, Fe, Ti, Mg, Y, and La, have been synthesized.[7] Despite this progress in alloy development, the fundamentals of glass forming ability and glass stability remain unclear. There are several factors which preclude establishing a comprehensive fundamental view of multicomponent BMGs. These include, first, the complexity of their atomic structure; second, the lack of appropriate mathematical formalism such as that similar to the symmetry group theory for crystals; and finally, the hybrid character of interatomic interactions in multicomponent BMGs (combination of different types of atomic bonding, mostly metallic and covalent). In addition to the fundamental problems of the structure and properties of BMGs, certain practical limitations hold back the industrial applications of these materials. For example, most BMGs lack ductility. Thus, improvement of ductility through tuning chemical composition is certainly an important goal of experimental and theoretical research.

One of the questions crucial to understanding physical properties of MG is the local atomic structure. Indeed, knowledge of the short-range order (SRO) in metallic glasses is important for understanding local topological and chemical ordering, the atomic size, and local strain effects. X-ray and neutron diffraction via pair-distribution function (PDF) analysis are the most straightforward methods to study the local atomic structure of metallic glasses. However, due to the one-dimensional character of experimental PDFs, the structural models obtained by simulations cannot be considered unique even in case of a good agreement between experimental and simulated PDFs. In short, a clear relation between structural models and physical properties is necessary for the validation of such models. An ability to simulate physical properties of MGs is important itself as it would greatly simplify the design of chemical compositions for MGs with pre-defined physical characteristics. In the case of a multicomponent MG, the application of traditional theoretical computational methods, such as classical molecular dynamics (MD), is difficult due to a necessarily large number of fitting parameters which are often impossible to obtain directly from experimental data. Thus, an alternative to classical MD is the first-principle methods such as *ab initio* MD, which virtually does not require any experimental information and, therefore, is especially useful for the simulation of multicomponent MG. Until recently, only relatively simple binary alloys were investigated by *ab initio* MD (Ref. 8) because of the high computational cost of this method. However, as was demonstrated in,[9] *ab initio* MD can be used successfully in studying a multicomponent MG.

Here, we report the results of the investigation of the local atomic structure of two series of multicomponent BMGs with general chemical formulas $Fe_{49}Cr_{15}Mo_{14}Er_1(C_xB_y)_{21}$ and $(Fe_xMo_y)_{76}P_{12}C_{10}B_2$ and present the results of *ab initio* MD simulations of the elastic properties in these systems on the basis of the obtained structural models. On the one hand, the series without phosphorus possess better glass forming ability in terms of the maximum diameter of the synthesized pattern (up to 6 mm vs 3 mm in case of alloys with phosphorus). On the other hand, samples with phosphorus demonstrate improved ductility. As we show in the following sections, a comparison of these two series of samples elucidates the role of particular elements in the formation of three-dimensional (3D) structure and their influence on physical properties of the compounds under study. Furthermore, the results of *ab initio* MD simulations and the Voronoi analysis of the obtained structural models allowed us to explain the chemical composition-related changes in physical properties.

II. SIMULATION DETAILS

The details of sample preparation and neutron-diffraction experiments can be found elsewhere.[10–13] The modeling was conducted using the VASP software[14,15] together with the projector-augmented wave method.[16,17] The Perdew-Wang generalized gradient approximation exchange-correlation functional[18] with Vosko-Wilk-Nusair spin interpolation[19] was used in order to take into account magnetization effects. The simulations where the temperatures of the glasses were below 1500 K were carried out with collinear spin polarization on Fe and Cr atoms in order to imitate the role of localized magnetic moments, which can be important even in the liquid state. In fact, alloys are not necessarily magnetic even at a high concentration of magnetic ions: long-range magnetic correlations can be suppressed due to several factors—in particular, as a result of spatial disordering. However, local magnetic correlations in the liquid state could affect the formation of the final atomic configuration of the glasses. At very high temperatures, local magnetic correlations in liquid are repressed by thermal vibrations, but at temperatures close enough to the solidification point, they should be taken into account in order to correctly describe a process of the structure formation. This is a reason why we used $T=1500$ K as a "critical point" below which spin-polarized calculations were performed: the melting point for these glasses is ~ 1200 K. At the same time, it should be noted that spin-polarized calculations are much more time consuming that spin-unrestricted ones. This is especially problematic in the case of glasses when we have a virtually random arrangement of atoms in a big enough glass/liquid cell. For this reason, at present it is difficult to clearly recognize correlations between the magnetic and other properties of these glasses in reasonable calculation time. This is a subject of future research.

The Monkhorst-Pack grids contained only the Γ point for the simulated liquid and amorphous cells of 100 atoms in a cubic box of ~ 1000 Å.[3] Periodic boundary conditions were applied to fill the 3D space. The time step in the MD calculations was 1 fs.

III. RESULTS AND DISCUSSION

A. Local atomic structure

The main purpose of this study is discussion and interpretation of structural data and elastic moduli measured recently for multicomponent MGs. Metallic glasses belonging to the same family (e.g., Iron-based MGs) reveal similar PDFs with minor variation in the position and intensities of the main peaks. Typical neutron PDFs,[20] g(r), for two particular compositions—with and without phosphorous additions—are shown in Figs. 1(a) and 1(b) as open circles. As a first approximation, they can be interpreted on the basis of the atomic size effect as follows.

The broad peaks on the PDFs reflect the glassy nature of the compounds in contrast to the sharp Bragg peaks in case of crystals. The low R region (<3.5 Å) corresponds to the short-range order or, in other words, to the first coordination shell. Two main peaks can be easily revealed in this interval. A simple interpretation of the positions and intensities of these peaks is based on the consideration of atomic radii and concentrations of constituent elements. Namely, the first peak with the center of distribution at ~ 2 Å is due to TM-Me (TM—transitional metal, Me—metalloid) pair correlations: the radii of the metalloid atoms are $\sim 0.8-1$ Å and the radii of the TM atoms are $\sim 1.2-1.4$ Å. Due to high concentrations of iron ($r(\mathrm{Fe}) \sim 1.25$ Å) in both series of samples, it is the Fe-Me pair correlations that mostly contribute to this peak and determine the position of the center of this peak at ~ 2 Å. It is seen that the intensity of this peak for samples with phosphorus is about two times lower than that for the compounds without phosphorus. This is because phosphorus atoms have the biggest radius among other metalloids in the compositions (~ 1 Å compared to ~ 0.8 Å for carbon and boron). Accordingly, the TM-P peak should be shifted to the right and overlap with the second main peak. The concentrations of carbon and boron in the compounds with phosphorus are roughly two times lower than in compounds without phosphorus, and this is a reason why the intensities of this peak are roughly two times lower for the compounds with phosphorus. The absence of any peaks lower than 1.6 Å points to the lack of close contacts between metalloid atoms or, at least, their inessential concentration in comparison with the correlations of other types in spite of the relatively high concentration of metalloids (up to 24 atomic per cent). Due to this fact, the 3D structure of MG can be considered as a superposition of metalloid-center clusters interconnected by faces, edges, and vertexes through metal (TM and rare-earth, RE) atoms. This is important for further discussion.

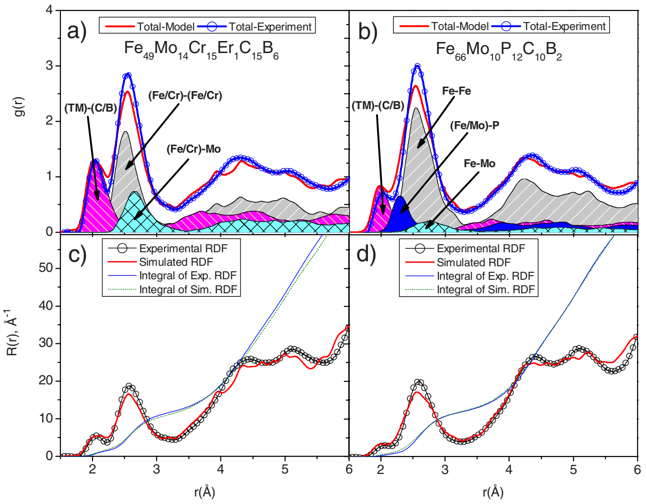

FIG. 1. (Color online) (a) Comparison of neutron PDFs and RDFs with the results of *ab initio* MD simulations. (b) Total neutron and simulated PDFs for $Fe_{49}Mo_{14}Cr_{15}Er_1C_{15}B_6$ and $Fe_{66}Mo_{10}P_{12}C_{10}B_2$ and corresponding partial contributions obtained by *ab initio* MD. (c), (d) Total neutron and simulated RDFs and corresponding integral intensities (total coordination numbers weighted by neutron-scattering factors).

The second main peak on the PDFs corresponds mostly to TM-TM pair correlations, although TM-P and TM-RE correlations give additional contributions to the wings of this peak. The distribution center at ~ 2.55 Å as well as its intensity is determined mostly by Fe-Fe correlations due to high iron concentration. It is evident that the most intense peaks are observed in the compounds with phosphorus. This can also be explained by a contribution of TM-P correlations to the intensity of the second peak. The weak halo at the right part of the main peak at ~ 3.2 Å corresponds to TM-Er correlations: it is absent for the compounds without Er. For compounds with higher concentrations of rare earths, this halo is more pronounced. The next coordination sphere ($R > 3.5$ Å) corresponds to the medium-range order (MRO), i.e., to arrangement of coordination polyhedra with respect to each other. In this region, PDF features become less resolved because of the ample quantity of partial pair correlations which bring contributions to the total PDF. It is clear that the difference in the positions and intensities of the peaks in this region for chemically different compositions is much smaller than that for the first coordination shell.

A more detailed interpretation of experimental PDFs can be obtained by investigating compounds with isotope substitution, which allows studying partial (or, more correct, differential) PDFs. However, these kinds of experiments are time consuming and usually expensive—especially in the case of multicomponent alloys, for which as many as n(n-1) measurements (where n is the number of different chemical species in the composition) have to be carried out. Another possibility is modeling atomic structure by using any theoretical approach and recovering PDF from the model. Toward this end, we used *ab initio* molecular dynamics based on the density-functional theory. Taking into account the high computational cost of *ab initio* MD, an appropriate initial atomic configuration should be found in order to obtain reasonable results in reasonable time. One of the possibilities is to use the atomic configuration of some crystalline compound with similar chemical composition. The crystallization of glasses during heating leads to the formation of competitive crystalline phases. These crystalline phases can be used to set up an initial atomic configuration for *ab initio* MD simulations. It is known that in the case of metal-metalloid iron-based MGs $(\mathrm{Fe,TM})_{23}(\mathrm{Me})_6$ crystal phase usually precipitates in the process of crystallization during heating the glass. At the same time, this phase serves as the competitive crystalline phase in the liquid-to-glass transition during quenching the liquid. Thus, the structure of this phase should be close to the structure of the glassy phase and may serve as a precursor of the glassy state.[21,22] The structure of this phase was used as the initial configuration for *ab initio* MD simulation. In order to have the correct chemical composition atomic positions in $(\mathrm{Fe,TM})_{23}(\mathrm{Me})_6$ structure were randomly populated by atoms in accordance with the exact chemical formula of the glasses under study. In order to have more realistic results at the first stage of simulation, structural relaxation at temperature as high as 2000 K was carried out. This allowed atoms to move from their initial positions to other positions more favorable from the energetic standpoint, thus decreasing the energy of the systems.

Results of *ab initio* MD simulations confirm qualitative conclusions about partial contributions to the total PDFs made above. The main partial contributions to total PDF obtained as a result of the MD simulations for two particular compounds—with and without phosphorus—are shown in Figs. 1(a) and 1(b), respectively. In particular, it can be seen that the Me-TM peak is split into two peaks corresponding to (C/B)-TM and P-TM contributions for the compound with phosphorus in accordance with suppositions based on taking into account the atomic size effect. Generally speaking, the description of structural features on the basis of atomic sizes is purely empirical (or even "geometrical") and should not be necessarily correct: the same chemical element in different compositions may have different atomic radii depending on the oxidation state. However, we did not introduce atomic radii as input parameters for DFT calculations. The obtained splitting of the Me-TM peak is a result of quantum-mechanical simulations involving the structure relaxation. Thus, it can be concluded that the applied theoretical method reproduces well the peculiarities of the electronic structure and spatial atomic arrangement even for these complex multicomponent alloys.

There is a certain discrepancy between experimental and simulated absolute intensities of the TM-TM peak as it is seen in Figs. 1(a) and 1(b). It should be noted that the absolute intensity of a PDF peak depends on several factors which include experimental uncertainties such as the diffractometer resolution and absence of a standard sample for the calibration of experimental data in case of glasses as well as an uncertainty in the choice of the "smearing factor" [the standard deviation in the Gaussian distribution used for spreading out the delta-function, $\delta(r\text{-}r_{ij})$, corresponding to a particular pair correlation between atoms i and j] at the simulation stage. However, absolute intensity cannot serve as a universal criterion of the correctness of the theoretical models. The integral intensities of the peaks of the radial distribution function (RDF), $R(r)=4\pi\rho_0 g(r) r^2$ (where ρ_0 is the average number density), determine coordination numbers which are important for understanding local atomic organization in glasses. Comparison of experimental and simulated RDFs and corresponding integrals ("total" coordination numbers weighted by neutron-scattering lengths), calculated as $I(x)=\int_0^x R(r)dr$, are shown in Figs. 1(c) and 1(d). It is evident that experimental and theoretical coordination numbers are quite similar in spite of some divergence between experimental and simulated RDFs. It should be emphasized that simulated glass cells contained as few as 100 atoms with periodic boundary conditions in comparison with $\sim 10^{23}$ atoms in real systems, and the difference in time scales between the theory and experiment is $\sim 10^3 - 10^6$ (a few picoseconds scale in *ab initio* MD vs nano- to microseconds in the experiment). Consequently, it would hardly be justified to expect an ideal agreement between the models and experimental results.

More detailed information about structural organization in MG can be obtained by using some special techniques such as the Voronoi analysis.[23,24] In particular, specific topological and chemical polyhedra can be deduced from the available structural model. It was shown that the coordination numbers for specific chemical elements in a composition mostly depend on their sizes and are very similar for different chemical compositions belonging to the same family.[9] However, the shapes and volumes of coordination polyhedra around the same chemical species are different due to the structural imperfectness of glasses. Nevertheless, such irregular polyhedra serve as main structural units ("elementary blocks") in these systems. For relatively simple binary alloys, it is possible to describe the medium range order as a combination of such "elementary blocks" and to track the peculiarities of their interconnection.[8] For multicomponent MGs, this task becomes extremely difficult because the number of possible connections between "elementary blocks" grows rapidly with the number of different chemical elements in the composition. We will not focus on this issue in this work. Instead, we will use results of the Voronoi analysis to estimate the relative strengths of atomic bonds for each particular chemical species in the compositions under study.

B. Elastic properties

From the application point of view, it is very important to have MGs with good mechanical characteristics. These include high mechanical strength, high fracture toughness, and high ductility. It is known that usually bulk MGs have poor ductility.[25,26] Therefore, an important problem is the enhancement of mechanical properties through understanding the correlation between chemical composition, atomic structure, and macroscopic physical characteristics. In the case of ordinary crystalline alloys, materials with better ductility frequently have higher Poisson's ratio, ν, or, equally, lower shear (G) to bulk (K) modulus ratio.[27–32] It was found that for the ductile MGs Poisson's ratio is higher than 0.32. The question if this value can be considered as the critical point for the brittle-to-tough transition is debatable. However, this rule gives, in principle, a chance to design MGs with improved ductility by the systematic adjustment of chemical composition. It was revealed that there is a general trend of ductility improving as the metalloid content in Fe-based MGs increases.[30] There are different types of atomic bonds in the metal-metalloid type of MG, mostly strong covalent bonds between metals and metalloids and relatively weak metallic bonds. It was assumed that the key point for understanding the dependence of ductility on metalloid content was the competition between these two types of bonds. According to Sheng *et al.*[8] the atomic structure of metal-metalloid MGs can be considered as a superposition of metalloid-centered clusters connected by weak metallic bonds, shearing vertices, edges and faces. *Ab initio* MD simulations[33,34] allowed an ascertainment to be made that increasing concentration of metalloids mainly leads to a growth of vertex-sharing clusters. On the other hand, it was found that shears are easily accommodated for clusters joined by metallic bonds and clusters which share vertexes and edges.[35] Thus, increasing metalloid contents leads to increasing the number of metalloid-centered clusters joined by metallic bonds through sharing vertexes. This provides a prerequisite for decreasing shear moduli, increasing Poisson's ratio and, consequently, improving ductility. At the same time, excessive amounts of metalloids may lead to an increase in the number of strong and directed covalent bonds with strong valence angle forces, which in turn leads to an increase in the shear modulus. Thus, in terms of ductility, an optimal amount of metalloids has to be determined. It was found that in the case of iron-based MG, this amount is ~20 atomic %.

For an arbitrary isotropic media, any elastic modulus (Young's modulus, Poisson's ratio, etc.) can be calculated if the values of any other two elastic moduli (or, equally, the longitudinal and transverse elastic constants, C_{11} and C_{44}) are known. We have attempted to simulate bulk and shear moduli within *ab initio* MD approach. Toward this end, a well-relaxed structure, for which atomic forces are close to zero and the system is close to the energy minimum point, has to be found. Thus, the first step of the simulation is full structure relaxation, at which both atomic coordinates and model cell parameters vary within the framework of a self-consistent approach. This brings the system to the energy minimum configuration (in the general case, a local energy minimum). As a result of relaxation, an atomic configuration $\{\vec{r}_1,\ldots,\vec{r}_N\}$, where $\vec{r}_i$ is the radius-vector of the atom i and N is the number of atoms in the model cell, and its energy at the bottom of the potential surface, $E_{\min}$, can be obtained. At the second step, it is necessary to investigate the dependence of energy on volume and shape of the model cell in order to simulate the bulk and shear moduli, respectively, using the relations $K=V(d^2E/dV^2)_{V_0}$ and $G=C_{44}=(1/3V_0)(d^2E/d\varepsilon^2)_{V_0}$ where V_0 is the volume of the model cell at $E_{\min}$ and ε is shear strain. In the case of bulk modulus, this procedure is straightforward. When the volume of the relaxed structure is slightly decreased and increased (by ~1%), ionic relaxation is repeated preserving the cell shape. As a result, three points of $E(V)$ will be obtained. These three points can be fitted by a parabola $E(V)=V_0+\alpha V+\beta V^2$ and then the bulk modulus, $K=2\beta V_0$, can be obtained. However, in the case of the shear modulus calculation, the situation is different. In spite of the cubic shape of the model cell, the actual atomic arrangement in the relaxed structure does not necessarily obey the isotropy condition. As a consequence, the simulation of the shear modulus cannot be done unambiguously: the cell can be distorted in different directions at a constant volume and results of such distortions can bring different values of the shear modulus. This is especially critical if the model cell is as small as we have (100 atoms in the cubic box of $\sim 10\times 10\times 10$ Å): due to anisotropy, the values of G, obtained under distortions in different directions, can vary considerably. Nevertheless, such calculations are useful in terms of general trends which can be obtained for different chemical compositions. For the calculations of shear moduli, the initial cubic cell was distorted in *ab*, *ac*, and *bc* planes. As a result three values of shear modulus (G_{ab}, G_{ac}, G_{bc}) for each particular compound were obtained. The results of bulk and shear moduli simulations are presented in Table I.

First of all, it is seen that the values of the simulated bulk moduli are in good agreement with the experimental data. It was shown in our previous paper[9] that the values of the elastic moduli slightly depend on the choice of the initial atomic configuration: an ensemble of nine independent initial atomic configurations of the same chemical composition was studied and it was found that the standard deviation does not exceed 5% of the average value among these nine configurations. It can be assumed that in reality this variation will decrease if longer relaxation is ensured at a high temperature (in the liquid phase). In other words, long relaxation in the

TABLE I. Comparison of experimental (Refs. 10 and 30) and theoretical (this work) values of bulk and shear moduli for the five particular alloys.

Compound	$K^{\mathrm{exp}}/K^{\mathrm{th}}$, GPa	$G^{\mathrm{exp}}/\langle G^{\mathrm{th}}\rangle(G_{ab},G_{ac},G_{bc})$, GPa
$Fe_{71}Mo_5P_{12}C_{10}B_2$	no data/190	$62.0\pm0.7/\langle 59.2\rangle(65.3,50.4,62.1)$
$Fe_{66}Mo_{10}P_{12}C_{10}B_2$	$176\pm4/187$	$66.1\pm0.7/\langle 65.0\rangle(62.4,62.8,69.9)$
$Fe_{49}B_0C_{21}Mo_{14}Er_1Cr_{15}$	no data/213	no data/$\langle 57.4\rangle(68.0,62.2,42.1)$
$Fe_{49}B_3C_{18}Mo_{14}Er_1Cr_{15}$	$200\pm4/203$	$80.2\pm0.7/\langle 70.2\rangle(69.8,82.4,58.5)$
$Fe_{49}B_6C_{15}Mo_{14}Er_1Cr_{15}$	$200\pm4/208$	$81.9\pm0.7/\langle 71.3\rangle(54.6,70.0,88.8)$

liquid phase draws together initially different atomic configurations making them unique for a particular chemical composition and thus decreasing the difference in the simulated physical characteristics. Therefore, the choice of the initial atomic configuration is important mainly in terms of the time of calculation: for a "good" configuration (i.e., when the model configuration is close to the "real" configuration for a particular alloy), the relaxation time can be much shorter than for a "bad" one but finally they become similar in terms of the arrangement of atoms and depend only on chemical composition.

On the other hand, it is evident that the bulk moduli for compounds with phosphorus are lower than for other compounds under study. This fact agrees with the results of,[30] where, in particular, the effect of substitution of boron and carbon by phosphorus is investigated. It was shown that the bonds between phosphorus and metals have a more metallic character in comparison with the stiff covalent bonds between carbon/boron and metals. Taking into account the relative weakness of the metallic bonds and the fact that roughly 50% of carbon/boron is substituted by phosphorus in those two particular compounds, it can be expected that on average this can lead to a decrease in the bulk moduli for compounds with phosphorus. In order to verify this supposition, we used the Voronoi analysis. Volumes of relaxed model cells for each particular compound were changed by ~5% preserving the shapes of the cells, the atomic relaxation was repeated, and then the Voronoi analysis was conducted for the energy minimum configuration and for distorted cells. Let us introduce the coefficients $k_i = \frac{V_{\mathrm{cell}}}{V_i}\frac{dV_i}{dV_{\mathrm{cell}}}$, which characterize the relative compressibility of the Voronoi polyhedron around the atomic species i (here V_{cell} is the model cell volume, and V_i is the volume of the Voronoi polyhedron around the atom i). According to this definition, for a homogeneous medium (i.e., when all the polyhedra have the same compressibility) $k_i = 1$ for any i. For an inhomogeneous medium, $k_i > 1$ for "soft" polyhedra (polyhedra with relatively soft bonds) and $k_i < 1$ for "tough" polyhedra (polyhedra with relatively strong bonds). As a result, averaging k_j's for each particular atomic species j (j=Fe, Mo, C, B, etc.), $\langle k\rangle = \Sigma_{j=1}^{N_j} k_j / N_j$, where N_j is the number of the atoms of the j type in the cell, allows one to determine the relative strength of the bonds on different chemical elements in the compositions. The dependence of the average k as a function of the chemical composition for five particular alloys with and without phosphorus is shown in Fig. 2.

It is evident that these dependences are very similar for different compositions and the trends are obvious. The compressibilities of Fe-polyhedra are close to 1 owing to high concentration of iron and, consequently, k(Fe) makes the main contribution to the average compressibilities of all the compounds. The softest polyhedra are around Er and the most rigid polyhedra are around C. At the same time, it is known that the RE/TM-C bonds are strong. However, the concentration of RE/TM–Me bonds in RE/TM centered polyhedra is ~20%. This means that 20% of stiff covalent bonds in such polyhedra cannot compensate 80% of relatively soft metallic bonds and, as a result, such polyhedra are relatively soft. Similarly, all the bonds inside the C/B-polyhedra are covalent and this is a reason why such polyhedra are less compressible. It is also seen that the compressibility of the P-polyhedra is close to compressibility of the TM-polyhedra. This confirms a conclusion about more metallic character of the P–(TM, RE) bonds in comparison with the C/B–(TM, RE) bonds. At the same time, more metallic character of bonds in compounds with phosphorus facilitates the shear accommodations as it was discussed previously. On the other hand, it can be assumed that a bigger polyhedron automatically means the higher compressibility of this polyhedron. The sequence of average volumes (or, equally, coordination numbers) of Voronoi polyhedra around various chemical elements can be written as $V(\mathrm{Er}) > V(\mathrm{Mo}) > V(\mathrm{Cr}) > V(\mathrm{Fe}) > V(\mathrm{P}) > V(\mathrm{B}) > V(\mathrm{C})$. For k_i this sequence is different: $k(\mathrm{Er}) > k(\mathrm{Fe}) > k(\mathrm{Cr}) \sim k(\mathrm{P}) \sim k(\mathrm{Mo}) > k(\mathrm{B}) > k(\mathrm{C})$. Taking into account the sequences of k_i being the same for different compositions, it can be concluded that this is not "a size effect;" rather, this diagram reflects the relative

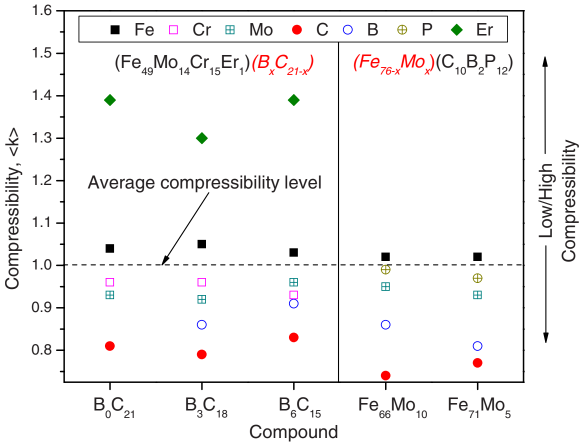

FIG. 2. (Color online) Relative compressibilities of Voronoi polyhedra around particular chemical species for the compounds under study.

strengths of bonds for different elements in the compositions.

As mentioned above, the situation with shear moduli is more complex. It is evident (Table I) that the values of G_{ab}, G_{ac}, G_{bc} can differ considerably for some particular compounds. Besides the described anisotropy of the model cell, it is clear that this effect is more pronounced for the compounds without phosphorus. This fact again can be interpreted in terms of the changing character of atomic bonding: "more metallic" compounds with phosphorus accommodate shears easier than compounds without it. On the other hand, well-oriented and strong covalent bonds between C/B and metals for the compounds without phosphorus should be more sensitive to the cell distortions in different directions. This may lead to possible anisotropy of G_{ab}, G_{ac}, and G_{bc}—especially in the case of compounds without phosphorus. We assume that this effect can be minimized if a larger model cell is used and, correspondingly, the anisotropy factor decreases. However, a theoretical approach used in this work does not allow using a substantially bigger model cell because the calculation time depends on the number of atoms in the model system, N, roughly as $\sim N^3$-N^4. In spite of the obtained dispersion of G_{ab}, G_{ac}, and G_{bc}, it is evident that the average values of shear moduli, $\langle G\rangle=(G_{ab}+G_{ac}+G_{bc})/3$, are in a reasonable agreement with experiments and reproduce correctly the main trend observed experimentally: a higher content of C/B leads to higher values of shear moduli. Moreover, it is surprising that such a small model cell allows one to estimate with reasonable accuracy both atomic structure and elastic moduli of these complex systems. This, probably, means that in reality the diversity of local atomic environments is very limited from the spatial point of view: the main structural and physical properties of MG can already be described by using a model cell as small as $\sim 10\times 10\times 10$ Å. On the other hand, this gives a hope that a combination of empirical Inoe's rules for finding good glass formers with the first-principle theoretical approaches similar to those used in this paper can serve as a useful tool for prediction and synthesis of MGs with enhanced characteristics.

IV. CONCLUSION

The atomic structure and elastic properties of multicomponent metallic glasses with the chemical formula $\mathrm{Fe_xTM_yMe_zEr_t}$ ($\mathrm{TM=Mo,\ Cr, Me=C,B,P,\ x+y+z+t=100\%}$), were interpreted through pair-distribution function analysis and *ab initio* molecular-dynamics simulations. It is shown that the main structural differences between particular compositions can be described in terms of the atomic size effect. The dependence of the elastic properties on chemical composition was studied on the basis of first principle calculations. Theoretically estimated bulk and shear moduli for the compounds under study are in a good agreement with the experimental values in spite of small model size. Changes of the ductility of the glasses induced by the substitution of carbon/boron by phosphorus were studied using the analysis of compressibility of Voronoi polyhedra around chemically distinct atomic species. These changes can be explained by changing the character of interatomic bonding from predominantly covalent to more metallic inside the metalloid-center clusters and could be appropriately used for enhancing the glass ductility.

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