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Atomic structure of an FeCrMoCBY metallic glass revealed by high energy x-ray diffraction

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Amorphous bulk metallic glasses with the composition Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} have been of interest due to their special mechanical and electronic properties, including corrosion resistance, high yield-strength, large elasticity, catalytic performance, and soft ferromagnetism. Here, we apply a reverse Monte Carlo technique to unravel the atomic structure of these glasses. The pair-distribution functions for various atomic pairs are computed based on the high-energy x-ray diffraction data we have taken from an amorphous sample. Monte Carlo cycles are used to move the atomic positions until the model reproduces the experimental pair-distribution function. The resulting fitted model is consistent with our ab-initio simulations of the metallic glass. Our study contributes to the understanding of functional properties of Fe-based bulk metallic glasses driven by disorder effects.

I. INTRODUCTION

Fe-based Fe-Cr-Mo-C-B-Y Bulk Metallic Glasses (BMGs) exhibit a homogeneous non-periodic structure on microscopic and macroscopic scales [1–4]. These alloys support compression strengths that are substantially superior to those of their crystalline counterparts [5–10]. Zhang et al. [11] have pointed out the promising potential of BMGs in functional and structural applications. Addition of rare-earths (RE) such as Y and refractory metals such as Mo enhance the glass-forming ability of Fe-based BMGs [1, 12–18], while Cr and Mo improve their corrosion resistance [19]. Interestingly, it was observed that glass formation in the Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} alloy is controlled not by the crystal nucleation rate, but by the crystal growth rate [20, 21]. The many interesting physical, mechanical, and magnetic properties as well as the high thermal stability of the BMGs are reviewed by Suryanarayana and Inoue [22]. Recently, Sun et al. [23] have shown that the surface of Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} behaves also as a catalyst for water dissociation and hydrogen evolution processes. These functional properties of materials often arise from competing phases [24], which break symmetries and generally promote disorder and heterogeneity. However, local bonding considerations still provide strong constraints and, as a result, the observed structures tend to contain local orderings and remain far from being completely random. Heterogeneity and disorder are important in connection with functional properties of materials. In CoFeB alloys, for example, disorder helps enhance spin polarization of the material [25].

Here, in considering Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}, our focus is on its microscopic structure. Since the atomic structure plays an essential role in understanding the atomic packing of BMGs [26], we compare the experimental Pair Distribution Function (PDF) [27] obtained using High-Energy X-Ray
Diffraction (HE-XRD) with the results of structural models obtained via Monte Carlo methods based on the Metropolis algorithm. Our approach unravels the atomic structure of this complex material in large unit cells and complements results obtained via first-principles Density Functional Theory (DFT) based computations on smaller cells [23]. Our study thus provides a baseline for structural models based on PDF analysis needed to understand the relationship between the atomic and electronic structures of Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2}.

II. TOTAL SCATTERING AND PDF FUNDAMENTALS

The total structure factor [28, 29], \( S(Q) \), is a function of the absolute wave number \( Q = |Q| = (4\pi/\lambda)\sin(\theta) \), where \( \lambda \) is the wavelength of the incident x-rays and \( \theta \) is the scattering angle. \( S(Q) \) is related to the coherent part \( \langle f^{coh}(Q) \rangle \) of the diffraction data [30] as follows:

\[
S(Q) = 1 + \frac{\langle f^{coh}(Q) \rangle - \Sigma C_i |f_i(\mathbf{Q})|^2}{|\Sigma C_i f_i(\mathbf{Q})|^2},
\]

where \( f_i(\mathbf{Q}) \) is the atomic scattering factor and \( C_i \) is the atomic concentration of atomic species of type \( i \). The reduced PDF, \( G(r) \), is given by the Fourier transform of \( Q S(Q) - 1 \):

\[
G(r) = \frac{2}{\pi} \int_{Q_{\text{max}}} Q |S(Q) - 1| \sin(Qr) dQ,
\]

and it can be expressed as:

\[
G(r) = 4\pi r [\rho(r) - \rho_0],
\]

where \( \rho_0 \) is the atomic number density of the material and \( \rho(r) = \rho_0 g(r) \) is the atomic pair density proportional to the PDF denoted by \( g(r) \). The peaks of \( G(r) \) and \( g(r) \) are associated with atomic distances. In order to improve spatial resolution of \( G(r) \), \( S(Q) \) must be measured with a higher \( Q \) cut-off \( Q_{\text{max}} \), which becomes possible with the high photon energies available in HE-XRD experiments. The radial distribution function (RDF) is obtained from \( g(r) \) as [31]:

\[
\text{RDF}(r) = 4\pi r^2 \rho_0 g(r).
\]

The PDF approach has been shown to be a useful method for determining structures of non-crystalline and disordered materials as well as nanoparticles [25, 30, 32–53].

III. EXPERIMENTAL DETAILS

The Fe_{48}Cr_{15}Mo_{14}C_{15}B_{6}Y_{2} ingot was prepared by arc-melting mixtures of pure metals (99.9 mass% purity), graphite C (99.95 mass% purity), and B (99.99 mass% purity) under an argon atmosphere. From this ingot, ribbon samples of about 20 \( \mu \)m thickness and 1 mm width were prepared by melt spinning onto a single copper roller at a roller tangential velocity of about 40 m/s. By using Mössbauer spectroscopy, we checked that there was no detectable signal from iron-oxide to rule out the presence of oxygen in our sample. Notably, if a high amount of oxygen is dissolved in a liquid, it would hard for the sample to be vitrified.

HE-XRD measurements were performed with a photon wavelength of 0.21 Å in the transmission mode at beamline BL04B2 of the Japanese synchrotron facility SPring-8. An ionization chamber was used for monitoring the intensity of incident x-rays, while four CdTe and three Ge detectors were used for monitoring the intensity of the scattered x-rays. Furthermore, a two-axis diffractometer installed at BL04B2 was used to cover low \( Q \) (small angle) region (≈ 0.1 Å\(^{-1}\)). The setup for HE-XRD at this beamline is described in more detail elsewhere [54, 55]. To achieve a high real-space resolution, the full 2\( \theta \) range for the analysis was used to obtain the structure factor up to 25.6 Å\(^{-1}\).

IV. REVERSE MONTE CARLO METHOD

For amorphous materials, the refinement of structural models is not straightforward due to the large number of atoms that need to be included in the model structures. The Reverse Monte Carlo (RMC) method [57] allows the determination of the atomic structures, which are derived directly from the experimental data. It involves searching for an atomic configuration that can reproduce the \( G(r) \) of the unknown structure within a designated \( \chi^2 \) tolerance. The RMC-generated configuration is thus a viable candidate for the structure of the target [58]. To limit the number of candidate structures, one can add additional constraints involving restraints-based bond lengths.

The experimental PDF was analyzed using the public domain software RMCPProfile [59] (version 6), see website rmcpprofile.org for details. The main input is the temperature that...
determines the mean-square atomic displacements; for other
details concerning the generation of initial structures, we refer
to the documentation of RMCProfile. Specifically, we model
the structure using a simulation box containing a 50 × 50 × 50 Å³ cluster with 5440 atoms, which is sufficient for captur-
ing important features of $G(r)$ [60].

We started our optimization process with a random arrange-
ment of atoms in the cluster, which was produced via the pro-
gram abinit build contained within the RMCProfile package [59].

The cut-off lengths were 2.20, 2.20, 2.30, 1.70, 1.80, 2.80,
2.20, 2.30, 1.70, 1.80, 2.80, 2.40, 1.90, 2.00, 3.00, 1.20, 1.40,
2.30, 1.40, 2.50, and 3.20 Å for Fe-Fe, Fe-Cr, Fe-Mo, Fe-C,
Fe-B, Fe-Y, Cr-Cr, Cr-Mo, Cr-C, Cr-B, Cr-Y, Mo-Mo, Mo-
pairs, respectively. Some polyhedral restraints follow from
these bond-length restraints and are described in the RMCPro-
file manual. During the optimization process, atoms were al-
lowed to move and swap within the simulation cube, where
the atomic moves were controlled by a Metropolis algorithm.
[These moves are restricted by the distance-window used.]

V. COMBINING RMC AND DFT

Typically, RMC method gives a snapshot view of about
10⁴ atoms. This number of atoms is much larger than
that used normally in DFT computations, although system
sizes amenable to first-principles treatment have been grow-
ing with the increasing availability of high-performance com-
puting resources.[61]. White et al. [62] has discussed ad-
vantages of combining DFT and PDF analysis. Recent stud-
ies [63, 64] have shown that RMC alone is sometimes not
sufficient to represent the full picture. RMC in conjunc-
tion with first-principles validation, however, can yield im-
proved structures. Accordingly, we have carried out spin-
polarized electronic structure calculations using the projected
augmented wave (PAW) method implemented in the Vienna
Ab-initio Simulation Package (VASP) [65–67]. The Gen-
eralized Gradient Approximation (GGA) parameterized by
Perdew, Burke, and Ernzerhof [68] was used to account for
exchange-correlation effects. Effects of gradient corrections,
which are included in the GGA, are important for capturing
magnetic properties of Fe [69]. A plane wave cut-off energy
of 500 eV was used. The k-points within the Brillouin zone
were generated using a uniform 2 × 2 × 2 Monkhorst-Pack [70]
mesh. A relatively small subset of our larger atomic cluster
that is representative of the stoichiometry of the actual ma-
terial was selected to execute DFT calculations. The atomic
structure was next relaxed, starting with coarse settings, fol-
lowed by increasing the precision and adding magnetism with
randomized initial magnetic moments. Total electronic energy
was minimized with a tolerance of 10⁻⁴ eV. The conjugate-
gradient algorithm was used to relax atomic structures until
all residual forces converged to within 0.1 eV/Å. A Gaussian-
smearing width of 0.05 eV (full-width-at-half-maximum) was
applied to the electronic states. Similar calculations have been
reported by Sun et al. [23], Yu et al. [26], and Kazimorov [71].

Our largest model used to carry out DFT computations to sim-
ulate $G(r)$ contained 212 atoms with an average density of
7.8 g/cm³ after relaxation, which is consistent with the corre-
sponding experimental values [20]. The selfconsistently de-
determed magnetic moments on the iron atoms are random,
and range from 0-1.45 $μ_B$, with most of them being less than
1 $μ_B$.

VI. RESULTS AND DISCUSSION

The experimental $S(Q)$ and $G(r)$ data are shown in Fig-
ure 1, which illustrates the decay of the oscillating features
over wide momentum and position ranges. Our $G(r)$ results
agree well with those of Liang et al. [60] based on the HE-
XRD experiments at lower 60 keV x-ray energy. In the lower
panel of Figure 1, $G(r)$ shows strong oscillations over 2 to
about 10 Å. It reflects the presence of well-defined short-range
order as well as signatures of amorphous traits [72]. Splitting
of the second peak in Fig. 2 has been explained by Clarke
and Jonson [56] to be a result of packing of spherical parti-
cles, where linear trimers of spheres are responsible for the
second subpeak and the first subpeak arises partly from the
face-sharing tetrahedra. Figure 5 of Ref. 56 illustrates the
three basic atomic configurations that give rise to dominant
contributions to the second peak in $G(r)$; these authors also
show that the first subpeak grows more than the second sub-
peak as the random icosahedral packing becomes denser. Pan
et al. [73] have shown that this splitting does not occur in the
liquid phase due to the lower density of the liquid compared to
the glass. Preference for icosahedral short-range order derives
from the tendency toward efficient atomic packing [74, 75] in
metallic glasses.

The PDF fit obtained through RMCProfile is shown in Fig-
ure 2. The agreement with experiment is excellent. In par-
ticular, the important splitting of the second peak is well re-
produced. Selected partial PDFs shown in Figure 3 demon-
strate that the first small peak at around 2 Å is mainly from
the contribution between the transition metal (Fe/Cr/Mo) and
C/B atoms, while the second peak, which is the main peak in
$G(r)$, arises mainly from the contribution of transition metals.
The wide double peak in the range of 4-6 Å appears from
hybridization effects between the various atoms. Our par-
tial PDFs are consistent with those of Kazimorov [71], who
discusses how the elastic properties are related to the atomic
structural features.

Figure 4 shows the optimized structure of the large cluster
that is compared with the corresponding
experimental values [20]. The selfconsistently de-
termed magnetic moments on the iron atoms are random,
and range from 0-1.45 $μ_B$, with most of them being less than
1 $μ_B$.

Our DFT-based $G(r)$ is compared with the corresponding
experimental results in Figure 6. A good overall agreement
is seen despite a relatively small number of atoms in the DFT
simulation. Our RMC model is also used as input of ab-initio
FIG. 2. Comparison of the experimental and RMC model $G(r)$. The experimental data are rescaled by the factor of 0.4395.

FIG. 3. Partial PDFs for selected atomic pairs.

MD simulations of the metallic glass performed on small periodic clusters, while providing non-periodic information on larger unit cells involving about 5440 atoms, which are useful for visualizing the nanoscale spatial heterogeneity of metallic glasses [76]. The $G(r)$ in Figure 6 varies linear in the low-$r$ region with a slope of $-4\pi\rho_0$, where $\rho_0$ is the average density, see Peterson et al. [77]. This slope is very well described by our DFT model.

VII. CONCLUSIONS

We have presented an inverse method in which total x-ray scattering is used to determine the structure of Fe-based bulk metallic glasses. The method yields an RMC structural model with a cluster of 5440 atoms in excellent agreement with the corresponding experimental data. This fitted model is consistent with our DFT-based simulations using a periodic cell containing 212 Fe atoms. Our atomic structure reveals the presence of spatial heterogeneity [76] in the glass with nanoscale density fluctuations. The densely packed regions host an icosahedral order [75] reflected in the splitting of the second $G(r)$ peak [56], while less dense regions exhibit tetrag-

FIG. 4. Optimized structure. The average coordination is 5.6 (most populous = 6). Color coding is as follows. Brown = Fe, Green = Cr, cyan = Mo, Black = C, Orange = B, Magenta = Y.

FIG. 5. 76-atom cluster cut from the center of our RMC computational cube. Color coding is as follows. Brown = Fe, Green = Cr, cyan = Mo, Black = C, Orange = B, Magenta = Y.

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of states for addressing the unique properties of amorphous steels, which involve a subtle interplay of metallic and covalent bondings [71].

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