Roles of local icosahedral chemical ordering in glass and quasicrystal formation in metallic glass formers

LETTER TO THE EDITOR

Roles of local icosahedral chemical ordering in glass and quasicrystal formation in metallic glass formers

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Abstract
It is well known that bulk metallic glass formers have a tendency to show local icosahedral chemical ordering. We argue that the frustration between this short-range bond ordering and the long-range crystalline ordering controls the fragility and the glass-forming ability of these liquids. Our model suggests that a system having a stronger tendency to show local icosahedral ordering should be less fragile and a better glass former. This scenario also naturally explains the close relationship among the degree of local icosahedral ordering in liquid, glass formability, and quasicrystal formability.

Liquid–glass transition phenomena are universally observed in various types of liquid, including molecular liquids, ionic liquids, metallic liquids, and chalcogenides. Among these, metallic glass formers, which require very rapid quenching for their vitrification, cannot be discussed on the same grounds as usual other glass-forming liquids, which can be vitrified even for slow cooling. However, the finding of bulk metallic glass formers (BMGFs) has completely changed the situation [1, 2]. Now we can discuss the physics of glass transition in the above-mentioned liquids on the same physical grounds in a universal manner. Indeed, BMGFs share many common features with other glass formers. Upon cooling, their viscosity increases in a non-Arrhenius manner and there is diversity in the steepnesses of the viscosity–temperature profiles, which is characterized by the fragility [3]. The density–density correlation function decays in two steps, with fast β-relaxation and slow α-relaxation. The latter is stretched and the stretched exponent β_K decreases with cooling below the mode-coupling T_c but becomes constant below the glass transition temperature T_g [4]. The value of β_K at T_g is found to be larger for a stronger glass former, which is consistent with the well-established correlation between β_K at T_g and the fragility [5].

Metallic glass formers have been expected to provide an ideal system for the description of the glass transition, since they should be comparable to a hard-sphere system. Contrary to the expectation that hard-sphere systems with centrosymmetric interactions should be fragile, however, BMGFs are found to belong to the group of strong glass formers. It is suggested that icosahedral short-range order (SRO) [6] exists in the molten state for BMGFs (see also [7, 8]

on recent developments) and plays an important role in their glass-forming ability. Even more interestingly, it was recently found that quasicrystals (QCs) grow during the slow heating or annealing of many BMGFs [9]. This raises an interesting question as regards the relation among the degree of local icosahedral ordering, glass-forming ability, and QC formation. In this letter, we consider this problem in the light of our two-order-parameter model of liquids.

Our two-order-parameter model of liquids [10–13] relies on the physical picture wherein (i) there exist unique locally favoured structures (LFSs) in all liquids and (ii) such structures are formed in a sea of normal-liquid structures and their number density increases upon cooling since they are energetically more favourable by ΔE than normal-liquid structures. The specific volume and the entropy are larger and smaller for the former than the latter, respectively, by Δv and $\Delta \sigma$. We identify the LFS as a minimum structural unit (symmetry element). For metallic glass formers, it should be an icosahedron, as first suggested by Frank [6]. To express such short-range bond ordering in liquids, we introduce the so-called bond-orientational order parameter Q_{lm} (see [14] for its definition). We take the normalized average of Q_{lm} over a small volume located at r, which we express as $\bar{Q}_{lm}(r)$. Then, its rotationally invariant combination can be defined as $Q_l(r) = [\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |\bar{Q}_{lm}(r)|^2]^{1/2}$. We can use this $Q_l(r)$ to define the local bond order parameter, which is the local fraction of the LFS: $S(r) \equiv Q_l(r)$. Note that $l = 6$ for an icosahedron [14]. Then the liquid state free-energy functional associated with the LFS is given by [10–13]

$$f(S) = \int dr \, [-\Delta G \, S(r) + J S(r)(1 - S(r))$$
$$+ k_B T \, (S(r) \ln S(r) + (1 - S(r)) \ln(1 - S(r)))],$$

where $\Delta G = \Delta E - T \Delta \sigma - \Delta v P$, J represents the cooperativity, k_B is the Boltzmann constant, T is the temperature, and P is the pressure.

Next we consider density ordering, which describes crystallization [10]. Density fluctuations ρ in the liquid phase indicating the instability toward the solid phase have a maximum at non-zero wavenumber q_0. This ordering is described by the following free-energy functional:

$$f(\rho) = k_B T \int dr \, \rho(r)(\ln \rho(r) - 1) - \frac{k_B T}{2} \int dr \, dr' \, \rho(r) c(|r - r'|) \rho(r'),$$

where $c(r)$ is the direct correlation function. This density ordering takes place near the melting point T_m, which is the liquidus temperature for metallic glass formers. Finally we include the effects of coupling between ρ and S and those of possible long-range QC ordering. Considering only the lowest-order coupling, we obtain the total free-energy functional of the system as

$$f(\rho, S) = f(\rho) + \int dr \, c\rho(r)S(r) + f(S) + f_{QC}. \tag{1}$$

Here f_{QC} represents a free-energy functional describing QC formation (long-range translational and orientational (Q_{6m}) ordering; see, e.g., [14] for its possible form). In the above free energy, there are new important effects of short-range bond ordering, which have not been considered in describing liquid–glass transition: (i) random-field effects of $S(r)$ on the density ordering; (ii) thermodynamic effects of short-range bond ordering stemming from $f(S)$; and (iii) long-range QC ordering (f_{QC}). Hereafter we discuss how these new effects affect the physical properties of BMGF.

First we consider effect (i). Our model tells us that $S(r)$ acts as random fields, which disturb the crystallization and aid vitrification [10][1], reflecting the frustration between the two

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[1] Our model is essentially different from previous frustration models (see [10, 12] for the details): in usual frustration models frustration is induced by the icosahedral ordering itself (the one-order-parameter model with internal frustration), while in our model it is induced by competing orderings.
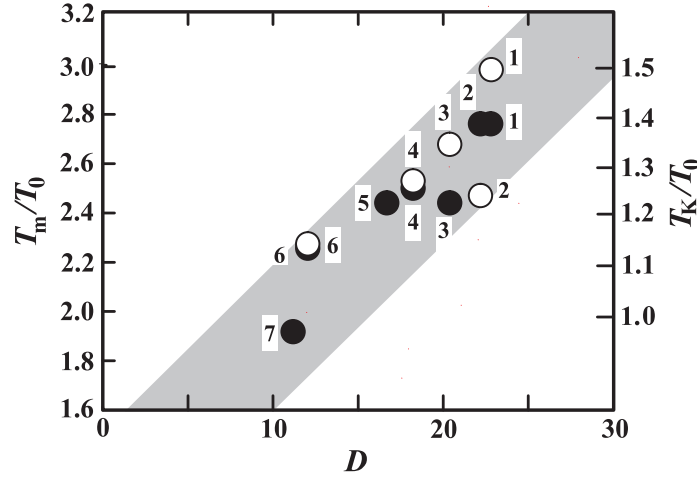
Figure 1. Correlation among T_m/T_0 (closed circles), T_K/T_0 (open circles), and D for metallic glass formers. 1: $Zr_{46.75}Ti_{8.25}Cu_{7.5}Ni_{10}Be_{27.5}$; 2: $Mg_{65}Cu_{25}Y_{10}$; 3: $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$; 4: $Pd_{40}Ni_{40}P_{20}$; 5: $Pd_{48}Ni_{32}P_{20}$; 6: $Cu_{47}Ti_{34}Zr_{11}Ni_8$; 7: $Pd_{77.5}Cu_6Si_{16.5}$.

order parameters. It should be noted [10] that the part of the free energy, $f(\rho) + \int d\mathbf{r}\, c\rho(\mathbf{r})S(\mathbf{r})$, which is responsible for vitrification is equivalent to that of Kirkpatrick and Thirumalai [15] if we regard $S(\mathbf{r})$ as a quenched random field and take the limit where the amplitude of $S(\mathbf{r})$ goes to zero. We note that this limit corresponds to the fragile limit in our model. It was also shown [15] that their theory is equivalent to schematic mode-coupling theory.

In our picture, disorder effects on density ordering set in only below $\sim T_m$. This reflects the change in the free-energy landscape from a simple to a multi-valley structure [10]. Note that $\delta f(\rho, S)/\delta\rho = 0$ starts to have multiple solutions below T_m due to random-field effects of $S(\mathbf{r})$. Thus, a transition from the Arrhenius to the non-Arrhenius behaviour (the onset of cooperativity) should occur around T_m. Upon further cooling, the system eventually becomes a spin-glass-like, non-ergodic state at the Vogel–Fulcher temperature T_0.

According to the scaling theory of Kirkpatrick *et al* [16] based on the part of the free energy in equation (1) $(f(\rho) + \int d\mathbf{r}\, c\rho(\mathbf{r})S(\mathbf{r}))$, the configurational (or state) entropy σ_{conf}, which is directly related to the density of the free-energy states, is obtained as $\sigma_{conf} = K_{conf}(T - T_K)/TT_K$. From the Adam–Gibbs relation [17], $\eta = \eta_0 \exp(C/T\sigma_{conf})$ (C: a constant); thus, we immediately obtain the Vogel–Fulcher law with $T_0 = T_K$: $\eta = \eta_0 \exp(\frac{DT_0}{T-T_0})$, where η_0 and D are constants. D $(=C/K_{conf})$ is known as the fragility index. Smaller D means that η increases more steeply upon cooling and a liquid is more fragile. A liquid with larger S suffers from stronger frustration effects. Thus, the distance between the onset of cooperativity, T_m, and its divergence temperature, T_0, increases with increasing S, which leads to larger D [10]. Thus our model suggests a positive correlation among the degree of icosahedral SRO (S), D, and T_0/T_m. This is confirmed in figure 1 for metallic glass formers.

Next we consider effect (ii). The equilibrium average ($\bar{S}$) can be straightforwardly obtained from $\delta f(\rho, S)/\delta S = 0$. For the case of $\bar{S}$, $J/k_B T \ll 1$ [10–13, 18], we obtain[2] $\bar{S}(T) \cong \exp(\frac{\Delta G}{k_B T})$ (see figure 2). Here we show that this short-range bond ordering

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[2] The validity of this relation is confirmed for water [11] and liquid silicon [12] and also for metallic liquids by numerical simulations [18]. At low temperature, however, the assumption used is no longer valid especially for a strong liquid. Furthermore, the cooperativity would even lead to a liquid–liquid phase transition [11, 13].
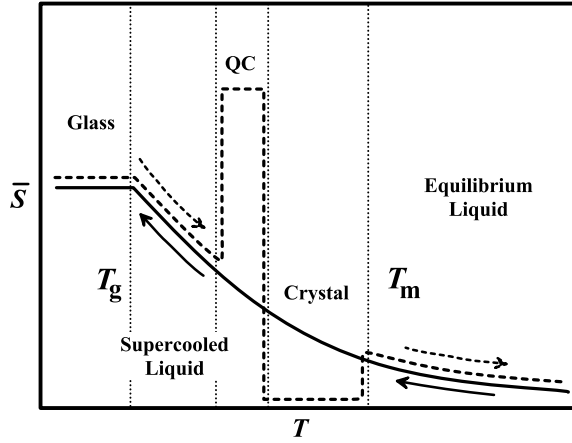
Figure 2. Changes of $\bar{S}$ upon cooling (solid curve) and heating (dashed curve). The QC can be viewed as an ordered state of S (or, more strictly, Q_{6m}).

affects the conventional picture even qualitatively. For example, the excess entropy should be modified by $-\Delta\sigma\,\bar{S}$, reflecting the short-range bond ordering. Thus, the excess entropy should decrease more rapidly than σ_{conf} upon cooling. This leads to the violation of the relation $T_0 = T_K$ [19]. Here T_K is the Kauzmann temperature, where the excess entropy of the liquid over the crystal becomes zero upon extrapolation. The deviation of T_K from T_0 should be larger for a stronger liquid with larger D, which can be confirmed in figure 1. This correlation has recently been confirmed for a wider variety of liquids [19]. Similarly, our model predicts [11] that many physical quantities such as the specific volume v_{sp}, the excess heat capacity of liquid over the crystal δC_P, and the electronic resistivity λ should have anomalous parts originating from the local icosahedral ordering: up to the lowest-order coupling, we obtain

$$v_{\mathrm{sp}} = v_{\mathrm{sp}}^{\mathrm{n}} + \Delta v\,\bar{S}, \tag{2}$$

$$\delta C_P = \delta C_P^{\mathrm{n}} + \Delta\delta C_P\,\bar{S}, \tag{3}$$

$$\lambda = \lambda^{\mathrm{n}} + \Delta\lambda\,\bar{S}, \tag{4}$$

where X^{n} represents the normal-background part and ΔX is the amplitude of the extra contribution from icosahedral SRO. Here we note that $\Delta v > 0$ and $\Delta\lambda > 0$ for BMGFs. This is supported by the volume expansion [20] and the increase of λ [21] upon formation of a QC, which should be characterized by large $\bar{S}$ (see figure 2). We also note that $v_{\mathrm{sp}}^{\mathrm{n}}$ and λ^{n} are both (almost linearly) increasing functions of T. Contrary to the normal behaviour of metallic liquids, however, $d\lambda/dT < 0$ for some BMGFs [22]. This can be naturally explained by our scenario. The proportionality of the anomalous part of δC_P to $\bar{S}$ is confirmed for water [11] and silicon [12], and also for metallic glass formers in numerical simulations [18]. According to our model, this increase of C_P upon cooling should be more pronounced for a stronger liquid, which has larger ΔG. Busch *et al* [23] found by their experimental studies that the increase of C_P upon cooling is more significant for stronger glass formers. This cannot be explained by the T-dependence of the configurational entropy $\sigma_{\mathrm{conf}} = \frac{C}{D}\frac{T-T_K}{TT_K}$, since its decrease upon cooling should be steeper for more fragile liquids with smaller D. Thus, the main contribution to C_P should come from the increase in icosahedral SRO in liquid upon cooling, and not from the decrease in σ_{conf}. Thus, the above argument can reasonably explain the stronger C_P-anomaly for stronger liquids (see equation (3)) [23], which also results in the larger deviation of T_K/T_0 from 1 (see figure 1) [19]. At this moment, there are few data that can be used for the qualitative
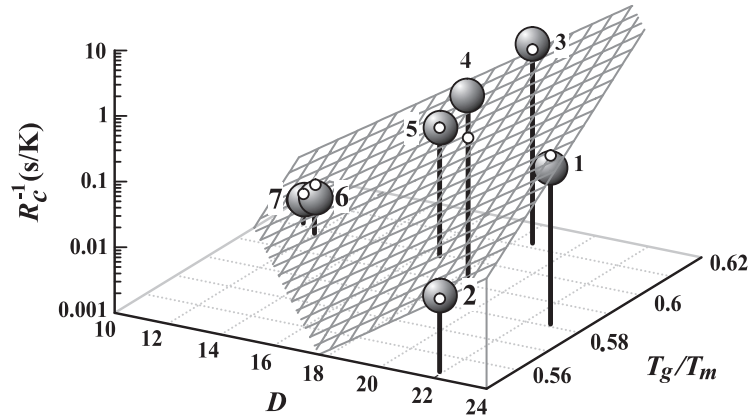
Figure 3. Correlation of R_c^{-1} with D and T_g/T_m for metallic glass formers (see figure 1 for the material number). We confirm a positive correlation between R_c^{-1} and D and also between R_c^{-1} and T_g/T_m. The latter is well known [24], while the former is newly established here. Note that there is no correlation between D and T_g/T_m (see the bottom plane), indicating the two factors are rather independent. The plane drawn with meshed grey lines, which was fitted to the data, is expressed as $-\log R_c = 0.266D + 45.1T_g/T_m - 32.5$. The large shaded spheres represent data points, while the small open spheres represent R_c predicted by the above relation. Since $\eta(T_m)$ is of the same order for these liquids, the difference in R_c should be induced solely by the thermodynamic factors.

check of relations (2)–(4). Thus, further experimental studies on the dependence on T, P of these quantities in a (supercooled) liquid state are highly desirable.

Here we consider how the local bond ordering affects glass formability. According to the classical theory [24], the nucleation frequency I is given by $I = \frac{k_n}{\eta} \exp[-\Delta F^c/k_B T]$, where k_n is a constant. ΔF^c is the free-energy barrier to nucleation of a critical nucleus, which is estimated as $\Delta F^c = 16\pi \gamma_{l-c}^3/(3\delta\mu)$ ($\delta\mu$: the Gibbs free energy of a supercooled liquid over the crystal per unit volume; γ_{l-c}: the interface tension between the liquid and crystal). Usually, it is assumed that $\delta\mu = \Delta H_f (1 - T/T_m)$, where ΔH_f is the enthalpy of fusion. According to our model, however, this should be modified due to the existence of LFSs as follows:

$$\delta\mu \cong \Delta H_f (1 - T/T_m) + \Delta G(T_m) \bar{S}(T_m) - \Delta G(T) \bar{S}(T). \qquad (5)$$

The downward deviation of $\delta\mu$ from the linear temperature dependence is indeed observed for various metallic glass formers [23, 25]. Furthermore, this deviation is larger for a stronger (better) glass former [23, 25]. According to our model, a stronger glass former should have larger $\bar{S}$. Thus, the above observation is quite consistent with our model. We also note that γ_{l-c} should be larger for larger $\bar{S}$. Thus, we conclude that the better glass formability is due to smaller $\delta\mu$ and larger γ_{l-c}, which are induced by *a stronger tendency to show icosahedral SRO (larger $\bar{S}$) of a stronger liquid with larger*[3] *D*. Glass formability is often characterized by the critical cooling rate R_c, which is the slowest cooling rate for forming a glassy state from a supercooled liquid without crystallization. Figure 3 clearly demonstrates a positive correlation between R_c^{-1} and D for metallic glass formers, which supports our model.

This prediction is also supported by the known experimental facts. Busch *et al* [26] pointed out that conventional metallic glass formers with rather poor glass-forming ability,

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[3] Our physical picture is further supported by the following fact [3]: BMGFs are characterized by lower thermal and electrical conductivity, which suggests a greater degree of electron localization in directional bonding. Thus, they should possess a higher degree of chemical SRO, which means a weaker thermodynamic driving force of crystallization in our model.
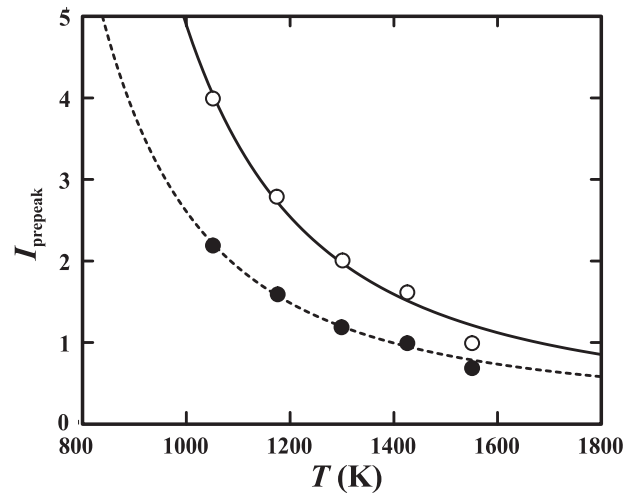
Figure 4. The temperature dependence of the intensity of the prepeak for $Al_{90}Fe_5Ce_5$ (open circles) and $Al_{90}Fe_{10}$ (closed circles). Curves are proportional to $\exp(\Delta G/k_B T)$. $\Delta G/k_B$ is estimated as 3930 and 3375 K, respectively, for the former and the latter.

such as $Zr_{40}Ni_{60}$, are in general fragile liquids judging from the fact that they show small heating-rate dependences of the glass transition. Considering this in combination with the strong nature of BMGFs, they pointed out that such a correlation exists for metallic glass formers. This argument was also supported by Perera and Tsai [27], who demonstrated that the better metallic glass formers are stronger, by examining many metallic glass formers.

Next we consider the structural evidence of the existence of icosahedral SRO. According to Sachdev and Nelson [28], icosahedral SRO should produce peaks at Q_0, Q_A, Q_B, and Q_C, which satisfy the relations $Q_A = 1.052Q_0$, $Q_B = 1.701Q_0$, and $Q_C = 2.0Q_0$. The existence of such icosahedral SRO in molten and glassy states is evidenced by the two subpeaks at the above wavenumbers Q_B and Q_C in the second peak of the structure factor $F(q)$ observed for BMGFs [7, 8]. Our prediction that the peak intensity of these peaks, which is proportional to the number density of icosahedral SRO ($\bar{S}$), should increase upon cooling obeying the Boltzmann factor and decrease with increase in P should be checked experimentally in the future. We also suggest that this feature should be more pronounced for a stronger liquid.

It is known that metallic glasses can be formed for a group of Al-based alloys with Al content close to 90 at.% in several Al–TM–RE (TM = transition metal, RE = rare-earth metal) systems [29]. However, it is quite unusual for metallic glasses with such high concentrations of the primary component (Al in this case) to be formable by thermal quenching, since they fail to satisfy the atomic size criterion for glass formability [30]. Zhang *et al* [31] studied the prepeaks for $Al_{90}Fe_5Ce_5$ and $Al_{90}Fe_{10}$ alloys, which are reminiscent of those for icosahedral chemical SRO, and found that their intensities increase upon cooling. The prepeak is interpreted as a diffraction peak broadening caused by fairly fine ($\sim$0.5–2.0 nm) icosahedral clusters. We find that the temperature dependence of the height of the prepeak $I_{prepeak}$ is well described by the Boltzmann factor ($\bar{S}$) for both alloys, as shown in figure 4. The higher activation energy for $Al_{90}Fe_5Ce_5$ means that the addition of Ce improves the interaction between atoms and aids the formation of icosahedral structures [31]. Thus our model suggests that this enhanced chemical SRO is the fundamental origin for the unusually good glass formability of these Al-based alloys.

In relation to this, we mention the origin of the boson peak [32]. We recently proposed that the boson peak is due to the localized vibrational modes characteristic of LFSs (icosahedral structures for metallic glass formers) and their clusters [33]. For checking this scenario, it is quite interesting to study the correlation between the intensity of a boson peak and that of a prepeak for the above Al–Fe–Ce alloy.

Finally, we consider the interesting problem of the relationship among local icosahedral ordering, glass formability, and QC formation [6–8, 14, 28]. Chen *et al* [34] recently reported the structural similarity between a supercooled liquid and an icosahedral phase in the $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ BMGF. They found that

(i) the effective activation energy of the transition from a supercooled liquid to an icosahedral quasicrystalline phase is much lower than that from a supercooled liquid to eutectic crystalline phases and

(ii) the activation energy of the transition from an icosahedral to a crystalline phase is almost the same as that of the transition from a supercooled liquid to a crystalline phase.

These facts strongly suggest a similarity in local atomic structure between the supercooled and the icosahedral phases.

As regards the relationship between glass and QC formation, it is worth mentioning a newly emerging paradigm for QCs. Steinhardt and Jeong [35] recently proposed that a QC is formed so that the density of a low-energy cluster ($\bar{S}$ in our terminology) is maximized. That is, a QC is a state of close packing of a single low-energy cluster (a LFS in our model). QC ordering is unconventional positional and orientational ordering of LFSs, allowing their overlap. We view the QC as a state maximizing icosahedral chemical SRO, or hierarchical ordering of the LFS (see figure 2). We suggest that local icosahedral chemical ordering in a liquid state is a prerequisite for QC ordering. We now have much evidence that metastable QCs are formed upon annealing for many BMGFs [9, 34]. Our model naturally explains why the composition region of BMGFs is closely related to the region of QC formation: $\bar{S}$ is large in the quasicrystal-forming composition region (large ΔG), which leads to the good glass formability and the strong nature of liquids. As long as the primary crystallization of the supercooled melt is the formation of intermetallic crystals, local icosahedral structures act as random fields against the crystallization. Thus, larger $\bar{S}$ makes liquid stronger. Formation of local icosahedral structures reduces the Gibbs free-energy difference between the supercooled liquid and the crystal and also increases γ_{l-c}, which makes crystallization more difficult. For a deeper supercooling, on the other hand, local structures of the liquid, which is characterized by large $\bar{S}$, are more similar to those of a QC. Thus, the interface tension between the liquid and the QC (γ_{l-qc}) becomes smaller than γ_{l-c}, reflecting the smaller values of $|\nabla S|^2$ and $|\nabla \rho|^2$. The symmetry of local icosahedral structures is consistent with that of QCs. Thus, QC formation is easier there. If the tendency to show icosahedral chemical ordering is too strong, however, a stable QC can be formed and liquid may become unstable against QC formation, which leads to poor glass formability.

In summary, we present a simple physical picture that naturally explains the close relationship among icosahedral short-range ordering, fragility, glass formability, and QC formation in metallic glass formers. Further experimental and theoretical studies are highly desirable to check the validity of this physical view.

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