Sharp Diffraction Maxima from an Icosahedral Glass

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We consider densely packed assemblies of icosahedra, such that icosahedral bond-orientational order is enforced throughout the sample. The peaks in the calculated diffraction patterns may be put in a one-to-one correspondence with the electron and x-ray diffraction patterns from icosahedral Al-Mn alloys, allowing the determination of the packing-unit size. We show that these maxima are not Bragg diffraction peaks, but have an intrinsic width, and may be understood as resulting from the interference between two or more characteristic lengths, as originally discussed by Hendricks and Teller.

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The discovery[1] that rapidly quenched samples of several transition-metal aluminum alloys produce electron diffraction patterns with "sharp" spots and icosahedral point symmetry has initiated a flurry of experimental and theoretical investigations. Long-range periodic translational order is incompatible with icosahedral point symmetry. While the existence of Bragg reflections, delta functions in reciprocal space, requires long-range positional order, this need not be periodic. This point has been exploited by several theories which model the icosahedral phase as space-filling structures which have long-range bond-orientational order and long-range, but nonperiodic, positional order.[2] A recent high-resolution x-ray powder diffraction measurement on samples of quenched Al_6Mn found that the icosahedral-phase diffraction peaks were not resolution limited.[3] Of the diffraction peaks which were sufficiently intense that the width could be measured, the half width at half maximum (HWHM) was in the range 0.009–0.04 Å^{-1}. This implies correlation lengths in the range of 100–300 Å, which must be reconciled with the electron-diffraction observation of bond-orientational order across grains $\sim 1\ \mu\text{m}$ in extent.

Previously, Shechtman and Blech reported the results of diffraction simulations from assemblies of icosahedra packed so as to preserve bond-orientational order throughout the sample.[4] The calculated diffraction patterns exhibit icosahedral symmetry, and contain strong, sharp peaks, a result which may seem somewhat surprising in view of the large apparent degree of disorder in the structure. They found "great similarity" between the calculated peak positions and the experimental electron-diffraction patterns, and proposed that these peaks arise from "the periodicity in the atomic planes."

In this Letter, we show that the diffraction pattern from such arrays is composed of interference maxima with different widths; although the sharpest are limited by the finite size of the present simulations, others are several times broader. Therefore, one cannot discuss the maxima as arising from coherent Bragg diffraction from periodic planes. Nevertheless, the calculated scattering pattern is in excellent quantitative agreement with the experimental peak positions, and qualitative agreement with the experimental peak intensities and widths. We show that these sharp maxima can be understood in analogy with the formalism developed by Hendricks and Teller for interference patterns from partially ordered layer lattices.[5] We therefore speculate that icosahedral alloys may be characterized as glassy structures in the sense that there is no long-range positional order, but that short-range chemical order is present, leading to a structure of densely packed units of locally icosahedral symmetry.

We first discuss the diffraction pattern generated by the packing of icosahedra vertex-to-vertex. We emphasize that the physical basis for such a model is clusters of atoms having icosahedral symmetry (i.e., a certain set of twofold, threefold, and fivefold axes) and not necessarily rigid clusters shaped like icosahedra. Starting from an initial seed, icosahedra were successively attached to a randomly chosen vertex, provided that each new icosahedron did not overlap another icosahedron already present in the array. Attaching the units so that their centers and common vertex are collinear enforces a degree of order on the model, so that each icosahedron has the same orientation. The growth process was continued until a cube of length $20a$, where $2a$ is the distance between two nearest-neighbor icosahedra sharing a vertex, could accommodate no further units. The packing fraction for the 1036 icosahedra packed into this cube is $\sim 50\%$.

In order to make contact with diffraction experiments, we imagine a point scatterer placed at the center of each icosahedron, and consider the structure factor $S(\mathbf{Q})$, which is proportional to the scattered intensity:

$$S(\mathbf{Q}) = |\textstyle\sum_j \exp(i\mathbf{Q}\cdot\mathbf{R}_j)|^2,$$

where the index j runs over all N sites in the structure. For a periodic structure, $S(\mathbf{Q})$ consists of a series of Bragg diffraction peaks with peak intensity proportional to N^2. These occur for wave vectors $\mathbf{Q}$ where all unit cells scatter coherently. In a finite sample of characteristic dimension L, the Bragg peaks have HWHM $w \sim \pi/L$.

Figure 1(a) shows the most intense local maxima of $S(\mathbf{Q})$ in one quadrant of a plane perpendicular to a twofold axis of the icosahedral units. In order to display the similarity between this calculation and the experimental electron-diffraction pattern, we have filled in the circles corresponding to the published diffraction spots in Fig. 2 of Ref. 3. In fact, spots corresponding to all of the open circles within the electron micrograph field of view are experimentally observed.[6] This striking agreement between the two patterns is also seen in planes perpendicular to threefold and fivefold axes. By a peak-to-peak match of the calculated and experimental peak positions, we determine that the distance between the centers of two adjacent icosahedral clusters in this model is $2a = 19.5$ Å. As expected, $S(\mathbf{Q})$ has icosahedral symmetry, within the sampling error of the finite-sized simulations.

In order to discuss the size and shape of these maxima in $S(\mathbf{Q})$, we have plotted this function along the twofold, threefold, and fivefold axes in the top traces of Figs. 1(b)-1(d). The strongest peaks of the simulation approach the maximum possible value of N^2, and have w of $0.15/a$. Therefore, the strongest peaks from the simulation are as intense and as sharp as those due to coherent diffraction from a periodic structure of the same size. On the other hand, the simulation exhibits weaker peaks, which can also be indexed to the electron-diffraction patterns.

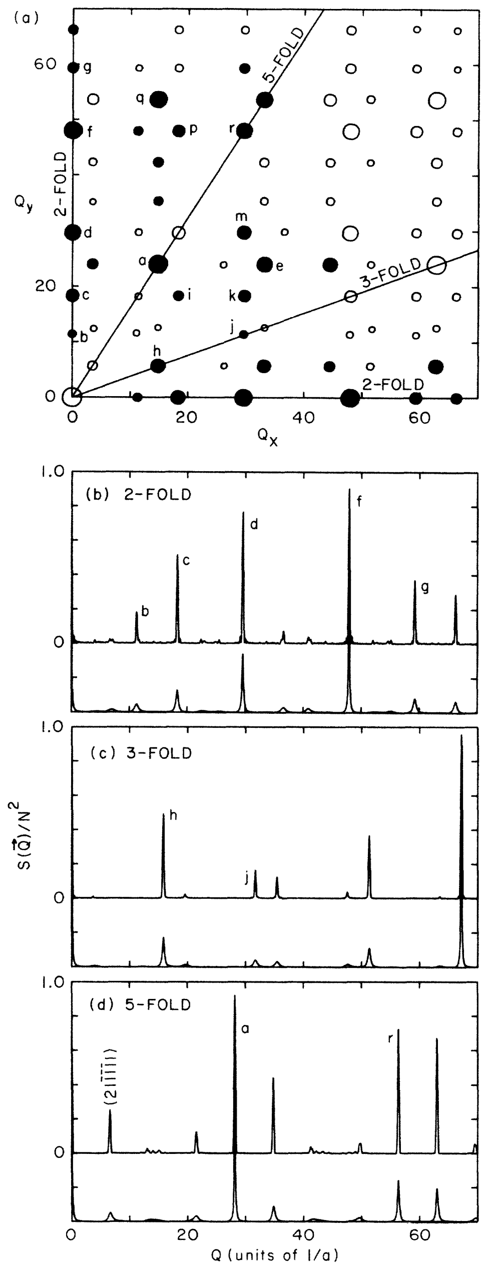

FIG. 1. (a) Intensities of diffraction maxima in one quadrant of the plane perpendicular to icosahedral twofold axis, calculated for a randomly grown network of icosahedral units, as described in the text. The area of each circle is proportional to the maximum calculated intensity. Filled circles and letters labeling spots are identified with the electron-diffraction pattern in Fig. 2(a) of Ref. 3. (b)-(d) Calculated ed scans along twofold, threefold, and fivefold axes. Upper traces are numerical results from the same simulation as Fig. 1(a); lower traces are calculated from the HT model, Eq. (1). There is an arbitrary scale factor between the two sets of calculations.

We have studied the behavior of several of the diffraction peaks as a function of simulation size. In order to obtain the peak shape, we performed an ensemble average over several symmetry-equivalent directions and several samples. We find that for sufficiently large simulations, the diffraction maxima have an intrinsic width that varies for different maxima. The maxima in $S(\mathbf{Q})$ evolve as a function of simulation linear dimension L as follows: For simulations smaller than π/w for a particular peak, the linewidth is $\sim \pi/L$, and the peak intensity is proportional to N^2. As the size of the simulation is increased beyond some correlation length for that peak, the width reaches a finite limit and the peak intensity is proportional to N. This crossover behavior, which is different for different peaks, shows that the scattering for sufficiently large samples is not coherent across the sample, and therefore the maxima cannot be described as Bragg diffraction. In contrast, models based on quasiperiodic or incommensurate order[2] predict delta-function Bragg peaks. This is apparently true even if the quasiperiodic pattern is distorted by local rearrangement of the units.[7] Therefore, our simulations provide the first theoretical framework for the observation of bond-orientational order over the full extent of a grain with the significantly shorter translational correlation lengths. The widths of several peaks are compared with the experimental values (from Ref. 3) in Table I, where it can be seen that the simulations produce peaks which are sharper than those observed experimentally.

Icosahedra of the same orientation can also be packed so as to share edges or faces rotated by 60°.[8] The edge model also produces sharp diffraction maxima with icosahedral symmetry, but the results cannot be indexed with the experimental electron-diffraction patterns. On the other hand, the face model produces a diffraction pattern that generally matches the electron-diffraction patterns, although the agreement is slightly worse than that of Fig. 1(a).[9] For example, peaks *b* and *j* do not show up as sharp maxima for any size simulation. Apart from this difficulty, this model may be indexed to the observed diffraction patterns if the center-to-center distance of peaked icosahedra is 10.9 Å. The structure of α-AlMnSi is essentially a bcc lattice of icosahedral clusters of atoms with their faces directed toward one another, precisely the same as the local configuration of this random-packing model. In that system, the center-to-center distance is 11.0 Å. This good agreement suggests an atomic basis for the randomly face-packed icosahedral units discussed here. The relationship between icosahedral AlMn and crystalline α-AlMnSi has been discussed from a different viewpoint by Elser and Henley.[10]

Having established that the model of random packing with icosahedral symmetry gives sharp diffraction peaks in agreement with the experimental results, it is natural to enquire as to the cause of these sharp maxima. As discussed above, they are *not* Bragg peaks resulting from coherent contributions of the scattered amplitude from each site in the sample, but may be understood on the basis of the following simple model.

We initially restrict our attention to wave vectors $\mathbf{Q}$ along the fivefold axis. The projection onto one particular fivefold axis of the vector joining any two "attached" icosahedra is either $\pm 2a$ or $\pm 2a\cos 63.43°$ $= \pm(4\tau-2)a/5$, where 63.43° is the angle between two adjacent vertices of an icosahedron (see Fig. 2). Consider a cluster of vertex-connected icosahedra. The projection along a fivefold axis of their separations consists of sums and differences of multiples of the two distances above. Because the simulated cluster was grown randomly, the sequence of displacements will generally appear to be random. This is similar to the model of scattering from partially ordered structures discussed by Hendricks and Teller (HT).[5] They considered a series of points distributed along a line such that neighboring sites are separated by distances d_1 or d_2 in a random sequence. Relatively sharp interference maxima occur at wave vectors Q such that $Q \sim 2\pi m/d_1 \sim 2\pi n/d_2$, with m and n integers, because a number of nearby sites all contribute nearly in phase to the scattered amplitude. For example, Fig. 2 shows how the diffraction maxima at $\mathbf{Q}=6.67/a$ $(21\bar{1}\bar{1}\bar{1}1)$ and $28.19/a$ (100000) along the fivefold axis arise from the interference between the two projected distances. HT give a closed-form expression for the general case of several displacements. If positive and negative displacements are equally probable, the scattered intensity per site is proportional to $(1+C)/(1-C)$, where $C=\sum_k f_k \cos(Qd_k)$, the sum is taken over all fundamental site separations $\pm d_k$, and f_k is the probability of occurrence of separation

TABLE I. Widths of icosahedral diffraction peaks. Experimental results are from Ref. 3; simulations and HT model are for vertex packings as described in the text. Entries of $\leqslant 0.003$ Å^{-1} have not saturated for the largest simulations performed: 109 454 sites in a cube of edge $100a$.

		HWHM (Å^{-1})	
Indices	Expt.	Sim.	HT
$(21\bar{1}\bar{1}\bar{1}1)$		0.008	0.040
$(2200\bar{1}1)$ *b*		0.007	0.041
(110001) *h*	0.018		0.021
$(1110\bar{1}0)$ *c*	0.014	0.004	0.025
(100000) *a*	0.009	$\leqslant 0.003$	0.009
(110000) *d*	0.022	$\leqslant 0.003$	0.015
(220002) *j*			0.041
(210001) *k*	0.04	$\leqslant 0.003$	0.029
(111000) *e*	0.021		0.018
(111100) *m*	0.020		0.021
(101000) *f*	0.021		0.009
(110010) *q*	0.020		0.013
(200000) *r*	0.04	$\leqslant 0.003$	0.018

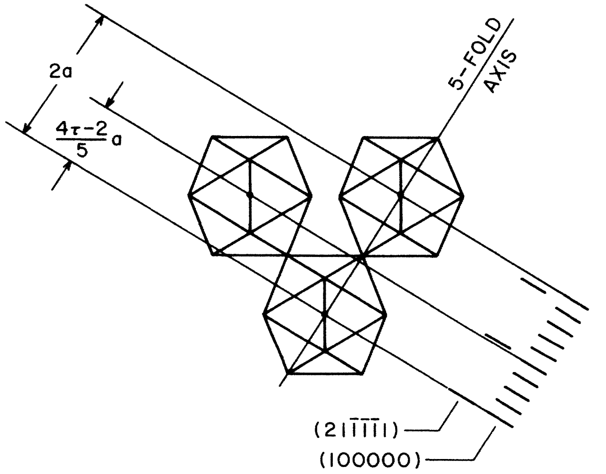

FIG. 2. Three vertex-connected icosahedra, illustrating the projected displacements along a fivefold axis.

$\pm d_k$.

In fact, along any given direction there are a finite set of displacement vectors which describe the projected separations of connected icosahedra. The HT analysis may be trivially generalized to the present three-dimensional problem by taking

$$C(\mathbf{Q}) = \tfrac{1}{6}\textstyle\sum_k \cos(\mathbf{Q}\cdot\mathbf{d}_k), \qquad (1)$$

where the sum runs over six independent vectors $\mathbf{d}_k$ pointing to the vertices of one icosahedron. The resulting function is plotted for $\mathbf{Q}$ along the twofold, threefold, and fivefold axes in the bottom traces of Figs. 1(b)–1(d). The strong similarity between the HT model and the numerical simulations shows that this simple model has captured the essence of the mechanism of sharp diffraction peak formation in the simulations. The HT model is similarly successful in predicting the peak positions for the face-packing configuration.[9]

Because the icosahedral vertex vectors $\{\mathbf{d}_k\}$ are incommensurate, there is no value of $\mathbf{Q}$ for which all of the cosines in Eq. (1) are unity. Consequently, each peak has finite maximum and width, depending on the degree of phase matching at its wave vector. It is of interest to compare the widths of the HT model peaks with the experimental values. Table I shows that the HT model gives peak widths qualitatively similar to those experimentally observed, although several times greater than those from the simulations. An important difference between the packing method used in the simulations and the HT model is the inhibition of overlap in the former, whereas the latter does not include a similar constraint. Physically, the HT model loses phase coherence in a smaller distance by allowing the possibility of going back and forth over the same neighborhood.[9] Consequently, the HT model yields a more disordered structure than the simulations.

We suggest that the general agreement between the HT model and the experimental peak widths in Table I is fortuitous, and regard this as an indication that the icosahedral alloys studied to date are more disordered than our simulations (e.g., through errors in the atomic formation of the icosahedral clusters). If our icosahedral glass model is correct, the simulations provide a lower limit on the experimental peak widths which might be obtained from more stable icosahedral alloys, as for instance, Al-Cr or Al-Mn-Si.[11]

Dense random-packing structures, introduced by Bernal,[12] form the basis for a group of models that have been used to describe the structure of metallic glasses. This concept has been modified to accommodate the presence of chemical short-range order, since it is now largely accepted that the *local* structure in these glasses strongly resembles that found in crystalline compounds of similar composition. Local icosahedral order in metallic glasses and liquids has been discussed recently,[13] and is apparently preferred for sufficiently small cluster sizes. In addition, crystal structures made up of periodic arrays of icosahedral units show that this form of packing of metal atoms can be favorable.[10] Here we have discussed a model for the icosahedral phase which packs these small clusters of atoms according to specific rules which enforce long-range icosahedral bond-orientational order. While they are not true Bragg peaks, the resulting strong interference maxima may be understood on the basis of a simple analytical (HT) model.

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