

## Is $\text{Al}_{86}\text{Mn}_{14}$ a quasicrystal or a cubic crystal?

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A theory is derived for a series of cubic structures which produce a nearly icosahedral system of reflections in compounds such as  $\text{Al}_{86}\text{Mn}_{14}$ . The different reflection widths and the nature of their deviation from icosahedral symmetry are explained.

Many elegant and comprehensive results obtained in the theory of quasicrystals during the last two years (see Refs. 1–3 and the bibliography cited there) make it possible to say with considerable certainty that quasicrystals must exist in nature. We recall that quasicrystals are usually understood to mean structures with long-range orientational and translational order which exhibit a noncrystallographic symmetry (e.g., icosahedral symmetry). We thus run into the natural question of whether the quasicrystalline structures do in fact occur in compounds such as  $\text{Al}_{86}\text{Mn}_{14}$  (the detection of icosahedral symmetry in the electronic reflections from such compounds<sup>4,5</sup> was the principal reason for the interest in quasicrystalline structures). We show below that the experimental data on x-ray and electron diffraction which are available for these compounds can be logically explained if it is assumed that these compounds are cubic crystals with a unit cell  $\sim 33 \text{ \AA}$  in size.

1. Let us first consider in purely geometric terms the question of the cubic and icosahedral reflections. It was shown in several studies<sup>1,2,5,6</sup> that the positions of the electronic reflections from  $\text{Al}_{86}\text{Mn}_{14}$  structures can be explained by assuming that the strongest reflections correspond to the reciprocal-lattice vectors  $\mathbf{G}_{\text{ic}}$  which are directed toward the icosahedron vertices and that the remaining reflections correspond to the linear combinations of  $\mathbf{G}_{\text{ic}}$  with integer coefficients. Such “apical”  $\mathbf{G}_{\text{ic}}$  have the form  $\{1, \tau, 0\}$  [i.e.,  $(1, \tau, 0)$ ,  $(0, 1, \tau)$ , etc.], where  $\tau = (1 + \sqrt{5})/2 = 1.618\dots$  (the so-called

TABLE I.

Interplanar spacing, Å		Reflection indices	
Observed reflections (Ref. 8)	Calculated reflections	Cubic reflections	Icosahedron (Ref. 6)
1.276*	1,273; 1,275	{26, 0, 0}; {21, 13, 8}	(101000)
1.495	1.49; 1.493; 1.496	{18, 13, 0}; {21, 5, 5}; {16, 8, 13}	(111000)
2.056*, 2.0624*	2.06; 2.068	{13, 8, 5}; {16, 0, 0}	(110000)
2.1681*	2.1681	{0, 8, 13}	(100000)
3.33	3.31; 3.34	{10, 0, 0}; {8, 5, 3}	(1110 $\bar{1}$ 0)
3.83	3.82; 3.87	{5, 5, 5}; {8, 3, 0}	(110001)

\* The strongest reflections

golden mean). Such a set of  $\mathbf{G}_{ic}$  corresponds to nonperiodic (quasicrystalline) structures with a long-range orientational and translational order. It is easy to see, however, that the vectors  $\{1, \tau, 0\}$  differ in direction from the vectors  $\{3, 5, 0\}$  by only 1%, from the vectors  $\{5, 8, 0\}$  by 0.5%, and from the vectors  $\{8, 13, 0\}$  by 0.2% (as we will see below, the numbers 3, 5, 8, 13 are not random). It is conceivable, therefore, that the structures observed in the case of  $Al_{86}Mn_{14}$  are in fact periodic structures and that they have a cubic symmetry which is close to an icosahedral symmetry, rather than a purely icosahedral symmetry.

We will show that the structure with the apical vectors of the type  $\{8, 13, 0\}$  indeed gives us the reflections observed in  $Al_{86}Mn_{14}$ . From the interplanar spacing of 2.168 Å, which corresponds to the apical vectors, we find the dimension of the cubic unit cell  $d = 33.09$  Å. It is easy to see that 30 edges of the "icosahedron" are formed by two types of vectors  $\{13, 8, 5\}$  and  $\{0, 0, 16\}$  with corresponding interplanar spacings 2.06 Å and 2.068 Å. Forming the linear combinations from the  $\{8, 13, 0\}$  vectors, we can index the remaining reflections (see Table I) which are close to the icosahedral reflections not only in interplanar spacings but also in the directions (for convenience, the icosahedral indices<sup>6</sup> are also listed in Table I). Like in quasicrystals, an "inflation" and "deflation" occurs in the structure under consideration; i.e., in addition to the principal icosahedron formed by the vectors  $\{13, 8, 5\}$  and  $\{0, 0, 16\}$ , we see the formation of a large number of larger and smaller icosahedra which differ by roughly a factor of  $\tau$ , e.g.,  $\{21, 13, 8\}$ ,  $\{0, 0, 26\}$  and  $\{8, 5, 3\}$ ,  $\{0, 0, 10\}$ , etc. A crystal, of course, contains the smallest icosahedron  $\{2, 1, 1\}$ ,  $\{0, 0, 2\}$  (in the  $k$  space!), whereas a quasicrystal has no smallest icosahedron because of the absence of periodicity.

An important point is that with the exception of  $\{8, 13, 0\}$ , there are several types of cubic reflections corresponding to the interplanar spacings observed by the x-ray diffraction methods (see Table I). As a result, the total angular width of these reflections is larger than that of  $\{8, 13, 0\}$ . For example, a single common peak is usually observed. This peak, which corresponds to 2.06 Å, is broader than the 2.168-Å peak to such an extent that the reflections  $\{13, 8, 5\}$  and  $\{0, 0, 16\}$  cannot be resolved<sup>6-10</sup> (Ref. 8, in which two peaks corresponding to 2.056 Å and 2.062 Å were observed, is an

exception). The broadening asymmetry<sup>9</sup> is also explained by the fact that the reflections {13,8,5} and {0,0,16} have different recurrence indices, 24 and 6. The most explicit evidence in favor of the cubic structure is the form and magnitude of the deviations from icosahedral symmetry observed in the diffraction of electrons from small ( $< 1000 \text{ \AA}$ ) domains.<sup>11</sup> In the case of diffraction in a cubic crystal, the fivefold axis is imitated by four reflections of the type {13,8,5} and by a single reflection of the type {0,0,16}, so that the length of one of the vectors is different from that of the other four vectors. In the case of the reflection {0,0,16}, this difference is less than the experimental errors, while for smaller reflections of the same series this difference is 2%, -3%, and 8% (the theoretical values for the corresponding reflections {0,0,10}, {0,0,6}, and {0,0,4} are 1%, -2.7%, and 7%; the minus means that the length is decreasing). For the reflections directed at an angle of  $\approx 72^\circ$  with respect to the reflections under consideration, there should be observed, and is indeed observed, a maximum angular deviation from the icosahedral symmetry (the experiment of Ref. 11:  $1^\circ$ ,  $-3^\circ$ ,  $> 3^\circ$ ; theory:  $0.5^\circ$ ,  $-1^\circ$ ,  $2.5^\circ$ ; the plus means that the reflections are converging).

2. Let us now determine which cubic space groups can the structure we are considering belong to. For this purpose, we will use the description of the (isotropic liquid)-crystal transition in the Landau theory, in which the order parameter are the Fourier harmonics of the density<sup>2,3</sup>  $\rho_G$ . Although an approach of this sort is clearly not suitable for a quantitative description of the crystallization process, there is the hope that the qualitative results, such as spatial symmetry of an ordered phase and the signs of the Fourier harmonics of  $\rho_G$ , are correct. Since we are considering the structure of the low-temperature phase, rather than the transition temperature, we can write the free energy  $F$  in the simplest form

$$F = \frac{1}{V} \int d\mathbf{r} (-\rho^3 + \rho^4) \\ = - \sum_{\mathbf{G}_1, \mathbf{G}_2} \rho_{\mathbf{G}_1} \rho_{\mathbf{G}_2} \rho_{-\mathbf{G}_1 - \mathbf{G}_2} + \sum_{\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3} \rho_{\mathbf{G}_1} \rho_{\mathbf{G}_2} \rho_{\mathbf{G}_3} \rho_{-\mathbf{G}_1 - \mathbf{G}_2 - \mathbf{G}_3}, \quad (1)$$

where  $V$  is the volume, and  $\rho(\mathbf{r})$  is the crystal density. Let us consider the functional (1) for the groups  $T^1-P23$  and  $T^4-P2_13$ , which are the subgroups of all the remaining cubic groups. Making use of the symmetry, we can reduce the number of independent  $\rho_G$  in (1): a) because  $\rho(\mathbf{r}) \rho_{-\mathbf{G}} = \rho_{\mathbf{G}}^*$ ; is real, b) because of the presence of the threefold axes  $\rho_{hkl} = \rho_{klh} = \rho_{lkh}$ , and c) because of the presence of the twofold axes in the group  $P23$   $\rho_{hkl} = \rho_{h\bar{k}\bar{l}} = \rho_{\bar{h}kl} = \rho_{\bar{h}\bar{k}l}$ , and the screw  $2_1$  axes in the group  $P2_13$   $\rho_{hkl} = (-1)^{h-k} \rho_{h\bar{k}\bar{l}} = (-1)^{l-h} \rho_{\bar{h}kl} = (-1)^{k-l} \rho_{\bar{h}\bar{k}l}$  (the coordinate axes are the same as in Ref. 12). We thus see that  $\rho_{0,0,16}$  and  $\rho_{0,8,13}$  are real in both groups,  $\rho_{0,13,8}$  is real in  $P23$  and imaginary in  $P2_13$ , and  $\rho_{13,8,5}$  and  $\rho_{13,5,8}$  are complex.

Retaining in (1) only those Fourier harmonics that correspond to the most intense reflections, we obtain  $F$  as a polynomial of fourth degree of the seven variables  $\rho_{0,0,16}$ ,  $\rho_{0,8,13}$ ,  $\text{Re}\rho_{13,8,5}$ ,  $\text{Im}\rho_{13,8,5}$ ,  $\text{Re}\rho_{13,5,8}$ ,  $\text{Im}\rho_{13,5,8}$ , and  $\rho_{0,13,8}$  ( $\text{Im}\rho_{0,13,8}$  for  $P2_13$ ). Minimizing this polynomial numerically, we see that some of the local minima of  $F$  correspond to cubic structures with a nearly icosahedral symmetry (for example,  $\rho_{0,0,16} = \text{Re}_{13,8,15} \neq 0$ ,  $\rho_{0,8,13} \neq 0$ , and the rest are zero). The symmetry increases to

$Pm3$  for the minima of the group  $P23$ , and the signs of  $\rho_{0,0,16}$  and  $\rho_{13,8,5}$  are positive, while the symmetry for the group  $P2_13$  increases to  $Pa3$  and the signs of  $\rho_{0,0,16}$  and  $\rho_{13,8,5}$  are negative [the sign of  $\rho_{0,8,13}$  is unimportant, since its change is equivalent to the transfer of the coordinate origin to the point  $(1/2, 1/2, 1/2)$ ]. The amplitudes  $|\rho_{0,8,13}|$  and  $|\rho_{13,8,5}|$ , which are comparable, are related as 1:0.44 in each group. The groups turn out to be the same for other choices of the apical vectors with one odd index and two even indices; for apical vectors with two odd indices ( $\{0,3,5\}$  etc.) the minima of  $F$  correspond to the groups  $Im3$  and  $I2_13$ .

The Landau theory thus implies that with any choice of the vertex vectors we can have two different cubic groups with a nearly icosahedral symmetry and with a different set of Fourier-harmonic phases. The "icosahedral" symmetry is conserved if the Fourier harmonics  $\{0,0,10\}$ ,  $\{8,5,3\}$  and  $\{0,0,26\}$ ,  $\{21,13,8\}$  are taken into account in  $F$ , whereas allowance for other, weaker Fourier harmonics listed in Table I and allowance for the quadratic and gradient terms in (1) leads to breaking of the icosahedral symmetry ( $\rho_{0,0,16} \neq \rho_{13,8,5}$ ).

3. Most of the indices of the observable reflections would seem to be either Fibonacci numbers  $u_n$  (1,2,3,5,8,13,21,...) or twice the Fibonacci numbers  $2u_n$ . First, the vectors  $\mathbf{G}$  of the type  $\{0,0,2u_n\}$ ,  $\{u_{n+1}, u_n, u_{n-1}\}$  are close to the edges of the icosahedron, while the vectors of the type  $\{0, u_n, u_{n+1}\}$  are close to its radii (the closer are the vectors to the radii of the icosahedron, the larger is  $n$ ). Secondly, the appearance of Fibonacci numbers (a less trivial point) is consistent with the Landau theory: Because of the recurrence relation  $u_{n+1} = u_n + u_{n-1}$ , even relatively few vectors  $\mathbf{G}$  of the type indicated above can form a large number of triangles  $\mathbf{G}_1 + \mathbf{G}_2 + \mathbf{G}_3 = 0$ , which accounts for the increase in importance of the cubic term in (1) and for the advantage of such structures from the standpoint of energy. It would therefore be logical to call the structures we are considering here Fibonacci crystals. In principle, there can be not only Fibonacci icosahedral crystals but also Fibonacci dodecahedral crystals (apical vectors  $\{0, u_n, u_{n+2}\}$  and  $\{u_{n+1}, u_{n+1}, u_{n+1}\}$  edges  $\{0,0,2u_n\}$  and  $\{u_{n-1}, u_n, u_{n+1}\}$ ). It is conceivable that the variety of diffraction patterns with fivefold axes observed in Al-Mn alloys corresponds to different Fibonacci crystals. An example of a Fibonacci crystal is an  $\alpha$ -Al-Mn-Si alloy with a symmetry  $Pm3$  close to  $Im3$ , in which the strongest reflections are the reflections<sup>10</sup>  $\{0,5,3\}$  and  $\{5,3,2\}$ ,  $\{0,0,6\}$ . The Fibonacci crystals seem to have a sequence of commensurate structures, which approaches an incommensurate quasicrystalline structure. If this is true, then the observable difference in the lengths of the orientational and translational ordering can be explained in terms of the breakup of a quasicrystal into domains comprised of Fibonacci crystals. The orientational order remains the same in this case (in the sense that the directions of the reciprocal-lattice vectors remain approximately the same), but the translational order is disrupted at distances on the order of  $|\mathbf{G}_{\text{cubic}} - \mathbf{G}_{\text{ic}}|^{-1}$ , i.e., at distances on the order of several hundred angstroms, a behavior which was observed experimentally. We wish to emphasize that Fibonacci crystals are naturally close to the icosahedral symmetry, so that there is no need to invoke twinning<sup>7</sup> in order to explain it.

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