

Icosahedral Symmetry

In his recent article "Icosahedral solids: A new phase of matter?" (27 Nov., p. 1242), Paul J. Steinhardt includes a section entitled "The case against conventional crystallography," in which he presents several arguments to support his contention that the evidence rules out the models of the so-called icosahedral quasicrystals of MnAl_6 and many other intermetallic compounds as icosahedral twins of conventional crystals. These include my own model (1), which was based on a cubic 820-atom crystal with eight icosahedral 104-atom clusters at the β -tungsten positions in the cubic unit of structure. I believe that Steinhardt's arguments are invalid.

With my model (1) the cubic crystals are so oriented with respect to a fivefold axis of the icosahedral quasicrystal grain that only $hh0$ primary reflections would occur on the fivefold-axis electron-diffraction photographs, with possibly a few other planes adventitiously in orientations permitting primary diffraction. I suggested (1) that some of the spots on the photographs are produced by double diffraction. Steinhardt states that double diffraction does not occur to any significant extent with x-rays and that "these peaks have been clearly observed in several independent powder x-ray experiments. . . . As a result, the specific models proposed thus far by Pauling have been ruled out."

I believe this conclusion is based on the fallacious assumption, as expressed by Steinhardt, that "Any peaks added by multiple electron scattering should not be found with x-rays." The presence or absence of an electron, x-ray, or neutron diffraction maximum (a peak) depends not only on the structure factor of the plane but also on the technique. Failure of a plane to produce a peak or spot is usually the result of a geometrical relation between the incident beam and the plane such that the Laue-Bragg conditions for diffraction are not satisfied. With monochromatic radiation and a stationary crystal in an arbitrary orientation, no plane can be expected to diffract. In the original Bragg technique and in the various rotating-crystal techniques, the crystal rotates into orientations satisfying the diffraction conditions. With my model of icosahedral twinning, the cubic crystallites are oriented to permit primary $hh0$ diffraction, and with my model of decagonal twinning they are oriented to permit all $hk0$ to show primary diffraction,

giving a fivefold-axis electron-diffraction photograph with many more spots (1). In the case of powder photography, there are for each plane some minute crystals with the proper orientation to permit diffraction, and accordingly peaks can occur that are ruled out for the stationary-crystal technique.

I shall not discuss Steinhardt's other arguments against the twinning model except to say that in my opinion they are all invalid. I have discussed some of them in other papers, mainly not yet published (2).

On the other hand, there is an increasing body of evidence supporting the twinning model. For example, the icosahedral quasicrystal Al_6CuLi_3 gives a fivefold-axis electron-diffraction pattern like that of MnAl_6 , but with a shrinkage in scale by 10%. I have analyzed the x-ray precession photographs of this substance and have found that the cubic unit of structure is larger than that of MnAl_6 , with 1088 atoms, eight 136-atom icosahedral clusters, in the β -tungsten positions in place of the eight 104-atom clusters of MnAl_6 . Also, I have found for decagonal Mn_2Al_7 , Fe_2Al_7 , and $(\text{Mn}_{0.7}\text{Fe}_{0.3})_2\text{Al}_7$ an orthorhombic unit with $a = 32.86 \text{ \AA}$, $b = 31.23 \text{ \AA}$, and $c = 24.80 \text{ \AA}$ containing 16 104-atom icosahedral clusters in positions slightly distorted from those for MnAl_6 . I have also found tetragonal structures for octagonal quasicrystals.

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REFERENCES AND NOTES

1. L. Pauling, *Phys. Rev. Lett.* **58**, 365 (1987).
2. ———, *ibid.*, p. 2120. In this paper the shift in positions of the spots is discussed.

Response: A viable multiple twinning model must explain the diffraction peaks observed in icosahedral solids in terms of the diffraction peaks of the twin crystallites. For any given model, the peaks can be divided into two classes. "Primary" peaks are ones that also appear in the diffraction patterns of one or more of the individual crystallites (1). "Secondary" peaks do not appear in the pattern of any one crystallite; they are only observed if there is multiple scattering (also called double diffraction) from two or more crystallites in succession.

Many multiple twinning models, including Pauling's, explain the peaks observed in electron diffraction from icosahedral alloys as a combination of primary and secondary peaks. A test for multiple scattering is to replace electron diffraction experiments from a single grain with x-ray diffraction from a powder containing many small

grains. The glib explanation given in my article is that significant multiple scattering is not expected in powder x-ray experiments because x-rays scatter much more weakly than electrons. "Yet, the peaks have been clearly observed in several independent powder x-ray experiments." This represents a serious blow for multiple twinning models. Although the approach is a conventional one for crystallographers, such a compact statement does not include the full logic of the argument. Since Pauling suspects that the argument is fallacious, I welcome the opportunity to discuss the issue in further detail.

The key features that distinguish powder x-ray from electron diffraction experiments are (i) in powder experiments, the scattering is from many small (1 to 10 micrometers in diameter), randomly oriented grains, whereas the scattering is typically from just one grain in electron diffraction; and (ii) the x-ray scattering length (2) is comparable to the entire sample thickness—orders of magnitude greater than the dimensions of a single grain—whereas the electron scattering length is less than the dimensions of a single grain. Primary peaks in powder x-ray diffraction come from the sum of the scattering from the individual grains. Because of the weak scattering of x-rays, the probability of scattering from any one grain is small; but there are many grains in the sample.

Multiple scattering contributions to secondary peaks are highly suppressed. First, the probability of multiple scattering within any single grain is extremely small because the grain size is small compared with the x-ray scattering length. Second, the probability of multiple scattering between two fortuitously oriented grains in the pulverized sample is not only small; but, if one averages over all possible relative orientations and positions of the grains, the sum over all multiple scatterings produces a smeared out "diffuse background" rather than a sharp secondary peak.

According to the quasicrystal model, all of the peaks observed in electron diffraction are primary peaks and should also be observed in a powder x-ray diffraction pattern with sufficient sensitivity. According to multiple twinning models like Pauling's, some peaks are secondary and, hence, should be greatly suppressed in amplitude in powder x-ray experiments. In the specific model of Pauling, the primary and secondary peaks are clearly delineated.

The experimental results for icosahedral solids are very clear, even more decisive than I described in my article. The electron diffraction peaks predicted to be secondary are unambiguously observed in powder x-ray experiments. In fact, they are significantly