Comment on a paper by Linus Pauling

PETER A. BANCEL*, PAUL A. HEINEY†, PAUL M. HORN*, AND PAUL J. STEINHARDT†

*IBM Research, Yorktown Heights, NY 10598; and †Physics Department, University of Pennsylvania, Philadelphia, PA 19104-6936

We agree with Dr. Pauling (1) that the small deviations from icosahedral symmetry observed in samples of Al_5Mn, Al_6CuLi_3, and $Al_{13}Cu_4Fe_3$ are inconsistent with the "simple" quasicrystal model (2). We also agree that, in principle, these imperfect samples can be described by a periodic crystal/twinning model. However, a requirement of twinning models is that the unit cell size must increase as the deviations from icosahedral symmetry diminish. For example, to explain the imperfect icosahedral AlFeCu samples obtained by K. Hiraga, Pauling suggests an extraordinarily large 52-Å unit cell, containing nearly 10,000 atoms. Yet, even this is too small to explain the "perfect" samples of AlFeCu reported by Bancel (3)‡ (after Pauling constructed his most recent model), which lack any observable deviations from icosahedral symmetry. A cubic crystal/twinning model would require a unit cell size >185 Å (425,000 atoms per cell) to account for the diffraction data from these samples.

The quasicrystal model, on the other hand, offers a straightforward and unified explanation for all of the samples. The deviations from icosahedral symmetry can be explained as due to phason strains (5, 6) quenched in the alloy during solidification, so that the observation of increasingly perfect samples is merely a consequence of less quenched strain during sample preparation (7). In this comment, we would like to discuss the similarities between the strained quasicrystal and multiple-twinning models and argue why the quasicrystal model may be the more natural approach.

Phason strains have been an important feature of quasicrystal theory because they can account for all the anomalies observed in the diffraction patterns of icosahedral alloys: (i) small shifts in peak positions from ideal icosahedral positions (6); (ii) peak shapes (7), including the peculiar triangular peaks observed in some samples (and described in Pauling's article); and (iii) finite peak broadening of Bragg peaks (7, 9). The first two anomalies are effects due to uniform phason strains, whereas the third anomaly is due to quenched random phason strains.

Briefly, quasicrystal elasticity theory predicts two types of elastic strains: phonon-type and phason-type (5, 6). By phonon strain, we mean the familiar elastic response of periodic crystals in which an applied stress distorts each unit cell from its equilibrium shape. Upon release of the external stress the strain relaxes via the propagation of phonons at the speed of sound. In a quasicrystal, one may have, in addition, a phason strain in which unit cells are rearranged but not distorted (10). Since all unit cells are identical in a periodic crystal, rearrangement does not change the structure, and, hence, there is no analogue of phason strain. In quasicrystals, however, in which there are two or more distinct types of unit cell, rearrangement changes the structure in a nontrivial way. Upon release of the external stress, phason strain relaxes by the diffusive motion of atoms, which restores the unit cells to the ground state configuration. The diffusive relaxation of phasons is much slower (occurring over hours, days, or even years) compared to phonon relaxation (occurring over mi-

croseconds) (11). These estimates lead to the prediction that phason strains should be observed in typical samples of icosahedral alloys even though the phonon strains may have relaxed away. It is then a straightforward generalization of crystal diffraction theory to derive the phason-induced peak shifts, shapes, and broadenings cited above (8).

It is no coincidence that Pauling can explain the first two anomalies in terms of a large unit cell crystal/twinning model, since such a model can exactly mimic the effect of uniform phason strains. An instructive analogy is to consider the effect of a small, uniform phonon strain along a (100) direction of a periodic cubic crystal. Each cubic cell is slightly distorted into some orthorhombic shape and the diffraction peaks are slightly shifted from perfect cubic symmetry positions to orthorhombic positions. If the strains were quenched, one could imagine two different explanations for the same diffraction pattern: (i) the sample is a cubic crystal with frozen-in phonon strains, or (ii) the sample is really an orthorhombic crystal. Similarly, uniform phason strain rearranges the unit cells globally such that icosahedral symmetry is broken and the ratio of different unit cell types is shifted from its ideal irrational value. The diffraction peaks for the strained structure are shifted from the ideal positions in a way such that, for any finite resolution measurement, the diffraction pattern can be explained via a nearby crystal rational approximant to the quasicrystal (8). In this case, it is impossible to tell on the basis of one diffraction pattern whether: (i) the sample is an icosahedral quasicrystal with frozen-in phason strains; or (ii) the sample is a very large unit cell crystal/twin.

However, a reasoned choice favoring (i) over (ii) can be made in either example if one can demonstrate that the materials pass additional experimental criteria: (a) Different samples of the same material may exhibit different diffraction peak shifts. (It would seem more reasonable to suppose that different samples had different frozen-in strains than to suppose a different large unit cell crystal model for each sample). (b) Annealing the sample might show that the shifts decrease, moving the peaks toward icosahedral symmetry positions. (c) The sample may be closely related to alloys that have been successfully prepared with perfect symmetry.

All of these criteria have been met in studies of icosahedral $Al_{13}Cu_4Fe_3$ and strongly suggest to us that this alloy should be identified as an icosahedral quasicrystal. Criterion (c) is satisfied since Bancel (3) has recently reported samples of $Al_{65}Cu_{23}Fe_{12}$ that exhibit no measurable deviations from the ideal icosahedral quasicrystal diffraction pattern. The long-range order is ≈100-fold times greater than in AlMn and AlCuLi phases, which pass criterion (a) but not (b) and (c). In particular, a cubic crystal/twinning model for icosahedral $Al_{65}Cu_{23}Fe_{13}$ would require an implausibly large unit cell size, >185 Å (425,000 atoms per cell), to account for Bancel's x-ray diffraction data (which are significantly higher in resolution than the diffraction data considered by Pauling).

Ultimately, we believe that Pauling's analysis can be meaningfully reconciled with the quasicrystal picture. His

‡Similarly perfect samples of icosahedral AlRuCu have been reported by Guryan *et al.* (4).

model of atomic clustering is based on a detailed understanding of the local interactions in intermetallic alloys and may explain the short-range order in icosahedral alloys. On the basis of the above arguments and the recent observations of Bancel (3), though, we believe that quasicrystalline order must be invoked to explain the observed long-range order in these materials. A unified model obtained by packing Pauling's atomic twin clusters into a quasicrystalline lattice may prove to be the best structural model for icosahedral alloys.

1. Pauling, L. (1989) *Proc. Natl. Acad. Sci USA* **86**, 8595–8599.
2. Levine, D. & Steinhardt, P. J. (1984) *Phys. Rev. Lett.* **53**, 2477–2480.
3. Bancel, P. (1989) *IBM Preprint*.
4. Guryan, C. A., Goldman, A. I., Stephen, P. W., Hiraga, K., Tsai, A. P., Inoue, A. & Masumoto, T. (1989) *Phys. Rev. Lett.* **62**, 2409–2412.
5. Levine, D., Lubensky, T. C., Ostlund, S., Ramaswamy S., Steinhardt, P. J. & Toner, J. (1985) *Phys. Rev. Lett.* **54**, 1520–1523.
6. Kalugin, P. A., Kitayev, A. Yu. & Levitov, L. S. (1985) *J. Phys. (Paris) Lett.* **46**, L601–L607.
7. Lubensky, T. C., Socolar, J. E. S., Steinhardt, P. J., Bancel, P. A. & Heiney, P. A. (1986) *Phys. Rev. Lett.* **57**, 1440–1443.
8. Socolar, J. E. S. & Wright, D. C. (1987) *Phys. Rev. Lett.* **59**, 221–224.
9. Horn, P. M., Malzfeldt, W., DiVincenzo, D. P., Toner, J. & Gambino, R. (1986) *Phys. Rev. Lett.* **57**, 1444–1447.
10. Socolar, J. E. S., Lubensky, T. & Steinhardt, P. J. (1986) *Phys. Rev. B.* **34**, 3345–3360.
11. Lubensky, T. C., Ramaswamy, S. & Toner, J. (1985) *Phys. Rev. B* **32**, 7444–7452.