Multiple-beam x-ray-diffraction studies of decagonal quasicrystals

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The problem under investigation is the structure of decagonal quasicrystals: the issue of centrosymmetry, and the effect of stoichiometry and composition. Phase information on structure factors is an important ingredient for structural investigations and the method used in this work is based on multiple Bragg scattering, a situation in which two or more Bragg reflections are simultaneously excited in the crystal. Three different but similar decagonal quasicrystals are investigated in this work: Al-Cu-Co, Al-Ni-Fe, and Al-Ni-Co. The lattice constants of all three quasicrystals are surprisingly identical. There are, however, differences in their structures. These differences are manifested in the phases of the Bragg reflections involved. What is measured, in a three-beam experiment, is the *triplet invariant* $\delta = \phi_{\mathbf{H}} + \phi_{\mathbf{P}-\mathbf{H}} - \phi_{\mathbf{P}}$, a linear combination of phases. The main reflection is called **P**, the simultaneous reflection is **H**, and $\mathbf{P}-\mathbf{H}$ is the coupling reflection. The structural differences between these seemingly isomorphous quasicrystals are evidenced by the different values of the triplet invariants for the same main and simultaneous reflections. In all cases we obtain δ values far from 0° and 180°, the only values compatible with centrosymmetric structures. We conclude that the decagonal quasicrystals investigated in this work are not centrosymmetric. [S0163-1829(98)00114-3]

I. INTRODUCTION

Although methods for recovering phase information are routinely employed for solving crystalline structures, their application to solving quasicrystalline structures has been tried but is still in its early stage of development.[1,2] A method for extracting *relative* phase information, multiple Bragg diffraction, has successfully retrieved phase information from crystalline[3] as well as quasicrystalline[4,5] structures.

A schematic representation of the multiple Bragg scattering technique is shown in Fig. 1. The main (**P**) reflection satisfies Bragg's law. Rotating the crystal about the scattering vector keeps the reflection excited. For certain values of Ψ, the azimuthal angle of rotation, a second set of planes may be brought into a position to diffract. In such a situation, the radiation from this simultaneous (**H**) reflection satisfies Bragg's law for the coupling ($\mathbf{P}-\mathbf{H}$) reflection so that the multiply diffracted radiation emerges from the crystal in the same direction as that from the main Bragg reflection. Monitoring the intensity as a function of Ψ yields visible modulations in the intensity of the **P** reflection as the **H** reflection is brought through the position where it is fully excited.

There exist several methods for extracting phase information from multiple Bragg diffraction. The method used in this paper utilizes the perturbation theory developed by Shen.[6] It is particularly well-suited for handling virtual Bragg scattering,[7] a situation in which the main reflection is weak, and the simultaneous reflection is strong but weakly excited. In such a situation, a large peak in intensity is observed when the simultaneous reflection is excited. As pointed out in Ref. 8, weak reflections are crucial to the detection of noncentrosymmetry. Hence, since the perturbation method both incorporates weak reflections and measures the interference between beams, it should be highly sensitive to the presence or absence of centrosymmetry. The amount of asymmetry visible on the peak's wings depends on the phases of the structure factors involved. Since the vectors $\mathbf{P}-\mathbf{H}$, **H** and $-\mathbf{P}$ sum to zero, the sum of their respective structure factor phases, $\phi_{P-H} + \phi_H - \phi_P$ is a structure invariant. In the perturbation theory, this constant is called δ, the ''triplet invariant,'' and it plays a critical role in determining how much asymmetry will be expected in the wings of the *umweg*.[9] Hence, using the perturbation theory to fit the experimental data yields values of δ. Since the phase information is retrieved from the wings of the *umwegs*, where the intensity is weak, and multiple scattering unlikely, crystal perfection is immaterial, and the method can be applied to mosaic crystals.[7,3]

II. MULTIPLE DIFFRACTION AND QUASICRYSTALLINE CENTROSYMMETRY

Symmetry operations that belong to a *periodic* structure's symmetry group carry the structure into an identical structure. For example, if a periodic structure possesses an n-fold rotational symmetry axis, the unrotated structure and the structure that is rotated by $2\pi/n$ relative to it will, when overlapped, exactly coincide out to infinity. Symmetry operations on quasiperiodic structures are less stringent; an operation that is a member of the quasiperiodic structure's symmetry group carries the structure into an *indistinguishable* structure.[10,11] Two structures are indistinguishable if any finite and bounded region in one can be found in the other. Hence, indistinguishable structures can be overlapped such that there is exact coincidence, but only over a bounded region. It is worthwhile to mention here that the issue of centrosymmetry in a quasicrystal has been analyzed in detail by de Boissieu *et al.*[12] Using a one-dimensional

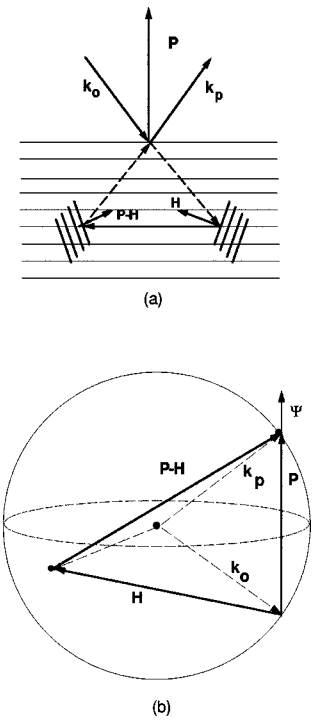

FIG. 1. Multiple Bragg scattering. (a) direct space, (b) reciprocal space.

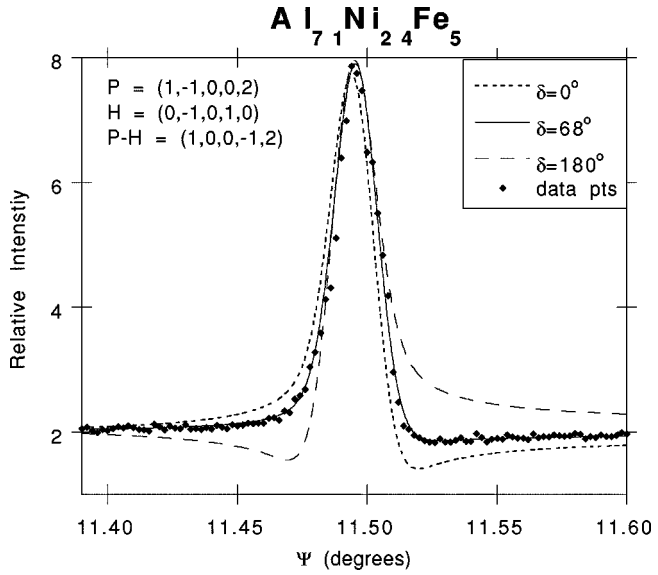

FIG. 2. Three-beam diffraction profile. The intensity of the **P** reflection is plotted vs the azimuthal angle Ψ, for rotations around the scattering vector **P**. The peak is due to simultaneous excitation of the **H** reflection. The angle Ψ represents the deviation (counterclockwise, looking against **P**) from the value corresponding to bisecting condition. This deviation is calculated using the orientation matrix of the crystal. More details are given in Ref. 5 (Sec. II).

model, projection from a two-dimensional periodic crystal, they arrive at the conclusion that a centrosymmetric crystal in two dimensions projects into an ''almost'' centrosymmetric quasicrystal in one dimension, containing centrosymmetric domains of bounded size which can be shown to be quasiperiodically distributed.

As shown in Ref. 13, indistinguishable quasicrystals are related by uniform phonon and phason shifts that leave the free energy unchanged. Equation (10) of Ref. 13 shows that the effect of these uniform shifts upon the electron density $\rho(\mathbf{r})=\Sigma_{\mathbf{K}}\mathbf{F}_{\mathbf{K}}e^{i(\mathbf{K}\cdot\mathbf{r}+\phi_{\mathbf{K}})}$, is to produce the indistinguishable density $\rho'(\mathbf{r})=\Sigma_{\mathbf{K}}\mathbf{F}_{\mathbf{K}}e^{i(\mathbf{K}\cdot\mathbf{r}+\phi'\mathbf{K})}$, where $\phi'_{\mathbf{K}}=\phi_{\mathbf{K}}+\mathbf{K}\cdot\mathbf{u}-\mathbf{K}^{\perp}\cdot\mathbf{w}$. The phonon shift is represented by $\mathbf{K}\cdot\mathbf{u}$ and the phason shift by $\mathbf{K}^{\perp}\cdot\mathbf{w}$. If a quasiperiodic structure is centrosymmetric, the process of inversion should produce an indistinguishable structure.

The relation to a three-beam experiment is as follows. If the quasicrystal is centrosymmetric, then $\rho(-\mathbf{r})=\rho'(\mathbf{r})$, which will be true only if $\phi_{-\mathbf{K}}=\phi'_{\mathbf{K}}$, or

$$\phi_{-\mathbf{K}}=\phi_{\mathbf{K}}+\mathbf{K}\cdot\mathbf{u}-\mathbf{K}^{\perp}\cdot\mathbf{w}.$$

Then, the triplet invariant can be written as

$$\begin{aligned}\delta&=\phi_{\mathbf{H}}+\phi_{\mathbf{P}-\mathbf{H}}-\phi_{\mathbf{P}}\\&=(\phi_{-\mathbf{H}}-\mathbf{H}\cdot\mathbf{u}+\mathbf{H}^{\perp}\cdot\mathbf{w})+[\phi_{-(\mathbf{P}-\mathbf{H})}-(\mathbf{P}-\mathbf{H})\cdot\mathbf{u}\\&\quad+(\mathbf{P}-\mathbf{H})^{\perp}\cdot w]-(\phi_{-\mathbf{P}}-\mathbf{P}\cdot\mathbf{u}+\mathbf{P}^{\perp}\cdot\mathbf{w})=-\delta,\end{aligned}$$

since the three vectors sum to zero in both direct and reciprocal space. Therefore, if the process of inversion on a quasiperiodic structure yields either an identical or an indistinguishable structure, a three-beam experiment should yield δ values of 0° or 180°.

III. EXPERIMENTAL

The alloys of the nominal compositions $Al_{68}Cu_{11}Co_{21}$, $Al_{71}Ni_{24}Fe_5$, and $Al_{72.5}Ni_{16.5}Co_{11}$ were produced by induction melting in a water-cooled Cu crucible. In order to obtain the single-decagonal structure the parts of the ingots were thermally annealed in a vacuum furnace and then quenched in water. The $Al_{68}Cu_{11}Co_{21}$ alloy was annealed for 133 h at 1000 ° C, $Al_{71}Ni_{24}Fe_5$ and $Al_{72.5}Ni_{16.5}Co_{11}$ for 120 h at 910 ° C. The single-decagonal structure of the samples was confirmed by metallographic procedures, powder x-ray diffraction and transmission electron microscopy. The compositions of the annealed samples were close to the nominal compositions of the alloys. A few crystallites (typically of 0.05 mm^3) were chipped from each sample with a razor blade, then individually fastened to glass fibers with Duco cement. Precession photography was used to determine the quality and orientation of the samples. The compounds used in this work represent structural variants of the decagonal phases belonging to the (Al-Co)-(Al-Ni) family.

None of the three samples showed the odd-*n* (where *n* is the indexing integer in the periodic direction) reflections in the (10000) photographs that were seen in other decagonal compositions, as in Fig. 4(a) of Ref. 14. Since the quasicrystals used in this experiment had all been subjected to prolonged annealing, and produced sharp diffraction peaks, it seems that those odd-*n* reflections must be viewed as the signature of lattice imperfections. All three samples had reciprocal-space lattice constants of $a^*=0.266$ Å^{-1} and $c^*=0.241$ Å^{-1} in the quasiperiodic and periodic directions, respectively.

Diffraction data were taken at beamline X-18A of the National Synchrotron Light Source at Brookhaven National Laboratory. For all experiments, the incident energy was tuned to 7600 keV with a Si(111) double-bounce monochro-

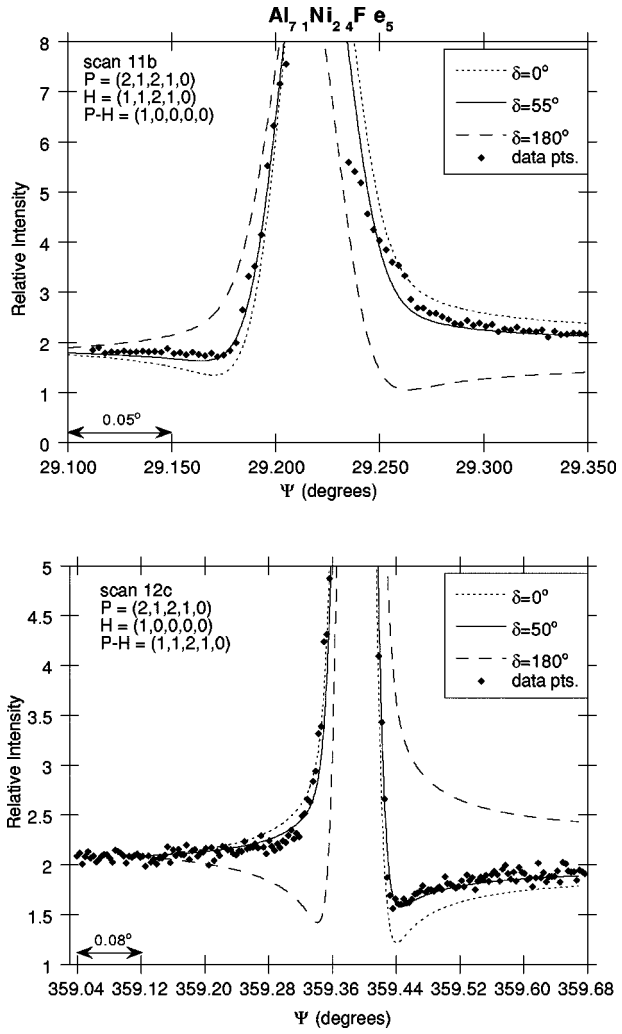

FIG. 3. The same as Fig. 2, except for the Miller indices of the **P** and **H** reflections. The two plots represent the same three-beam situations, because the **P** reflection is the same, and the Miller indices of the simultaneous and coupling reflections (**H** and **P**-**H**) are interchanged. The angles Ψ do not differ by 180° because in one case the node of the simultaneous reflection is *entering* the Ewald sphere, in the other case it is *exiting* the Ewald sphere. The two three-beam situations are physically identical.

mator. To minimize horizontal beam divergence at the sample position, no focusing mirror was used. Typical rocking curve widths were 0.02° full width at half maximum.

IV. RESULTS

The indexing scheme used in this work is described in Ref. 15. Results of the Al-Cu-Co system have previously been published.[16] Figures 2 to 5 show some of the azimuthal profiles obtained for the Al-Ni-Fe and Al-Ni-Co systems. All profiles were obtained by convoluting the theoretical fit given by the perturbation theory with a Gaussian smearing function. Figures 3 and 5 show profiles that are related by a 180° rotation about Ψ. Such a pair of plots should have the same δ values, as discussed in the Appendix of Ref. 17. Within experimental error, this is what was observed. At least five azimuthal profiles were obtained for each of the three samples. All of the profiles were best fit with δ values

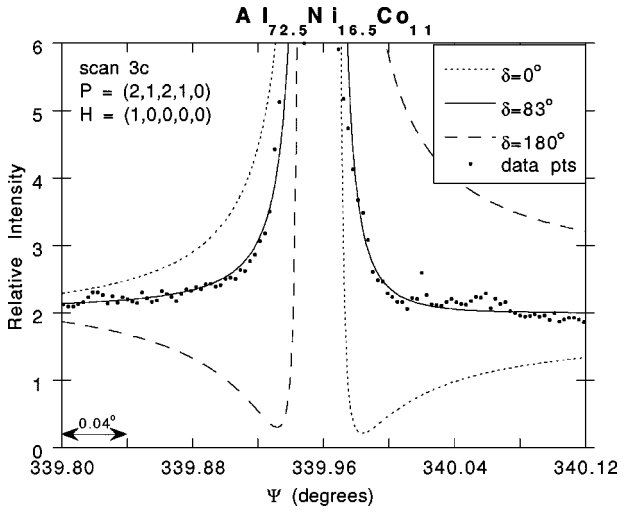

FIG. 4. The same as Fig. 2, except for the Miller indices of the reflections involved, and for the composition.

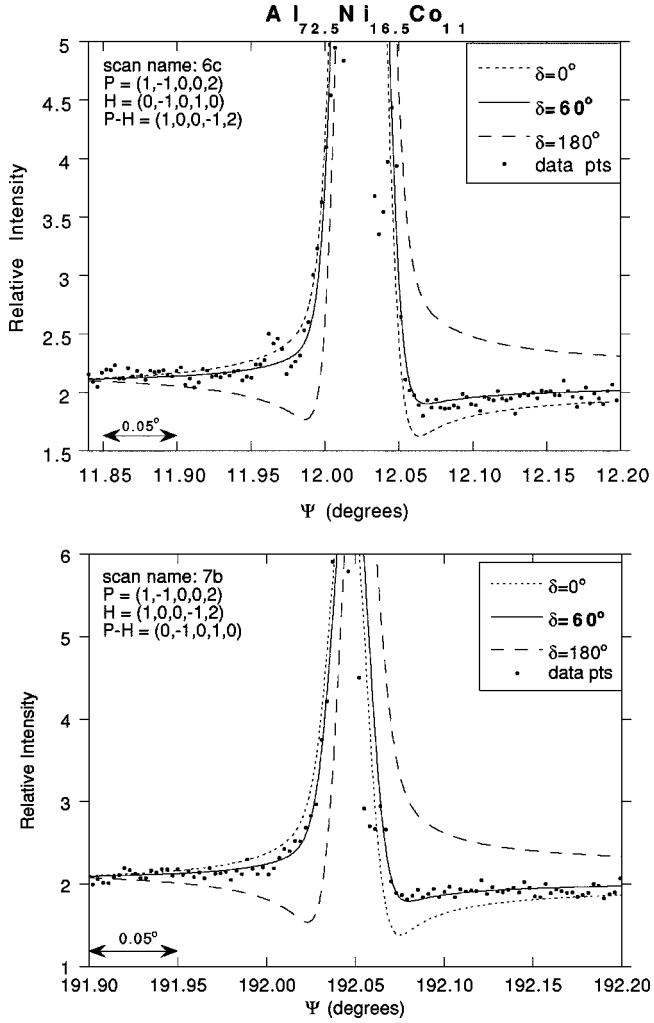

FIG. 5. The same as Fig. 2, except for the composition. The top profile has the same Miller indices as in Fig. 2. The bottom profile has the indices for the simultaneous and coupling reflections interchanged. In this case the Ψ angles for the two plots differ by 180° (with good approximation).

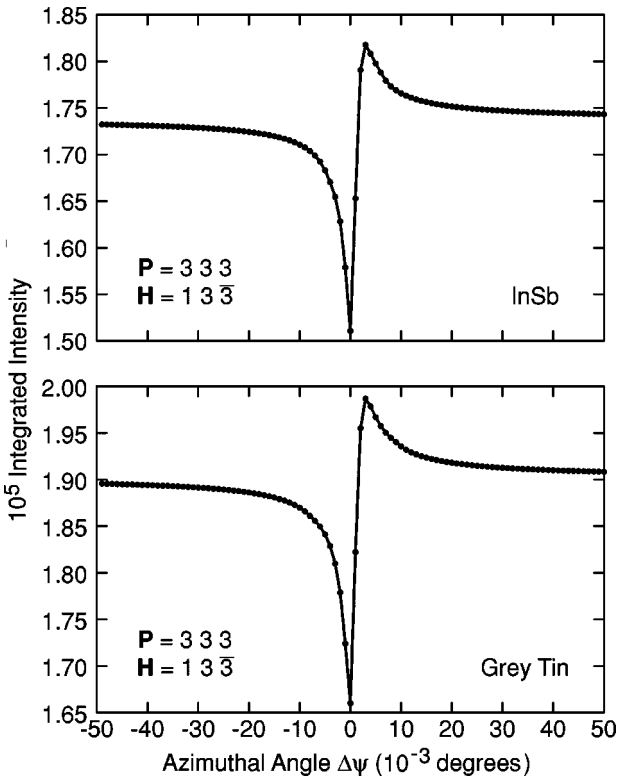

FIG. 6. Three-beam azimuthal profile for InSb and grey tin. All reflections involved are strong and of comparable intensity. The plots were computed using dynamical theory without approximations (Ref. 24). The two profiles are almost identical. The experimental values of the thermal factors for InSb are from Ref. 25. The experimental values of the thermal factor for grey tin and for the (222) structure factor are from Ref. 26. The points represent values for which actual computations have been performed. The solid lines are guides to the eye.

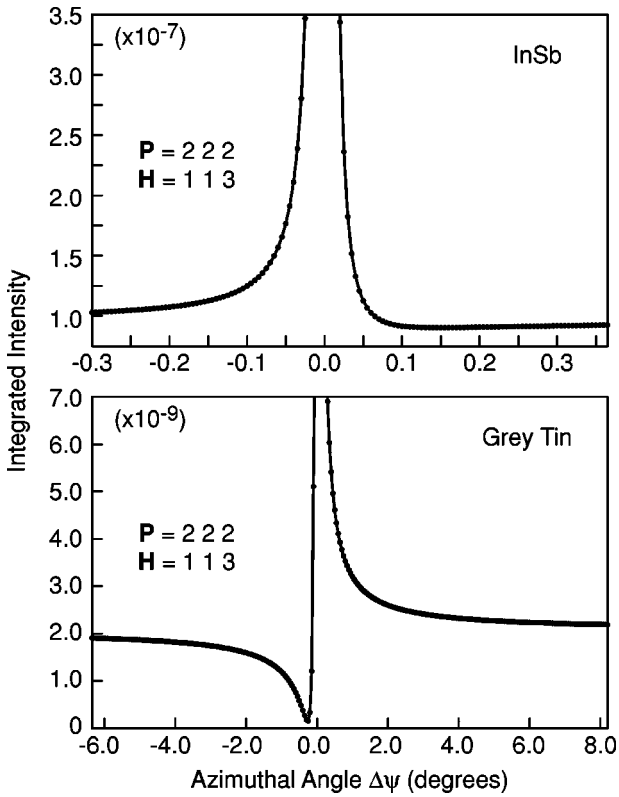

FIG. 7. The same as Fig. 6, except that the **P** reflection is very weak. The triplet invariant for the plot of InSb is 83.1° It would be 90° if absorption was neglected. Since the asymmetry effect is proportional to $\cos\delta$ (Ref. 6), the top profile is slightly asymmetric. The difference in shape between the top and bottom profiles is obvious. It is due to the slight departure of InSb from centrosymmetry.

far away from 0° or 180°, indicating that none of the samples is centrosymmetric.

The multiple diffraction experiments also revealed some qualitative differences between the samples. In general, the *umweg* peak intensities in the Al-Cu-Co system were higher than the equivalent peaks observed in the Al-Ni-Fe and Al-Ni-Co systems. Also, the latter two systems did not display the small side peaks that were observed in the strongest *umwegs* in the Al-Cu-Co system (see Fig. 2 of Ref. 16).

V. DISCUSSION

This observation of noncentrosymmetry is not in agreement with the Kossel-line observations of Schetelich *et al.* on $Al_{62}Cu_{20}Co_{15}Si_3$,[18] and with the structure models[19] that were deduced from Patterson analysis.

Our observations and conclusions are also in disagreement with recent results obtained by three-beam diffraction experiments similar to ours,[20] pointing to centrosymmetry. There seems to be a difference in methodology between our approach (virtual Bragg scattering, described in the introduction) and the method used in Ref. 20, in which strong reflections of comparable intensities were used. It was pointed out in the introduction that weak reflections are most sensitive to small departures from centrosymmetry.[8] The effect can be dramatically seen when considering two crystals of similar structure: InSb and grey tin. The latter is a diamond structure, centrosymmetric, with $Z=50$. In InSb the two fcc sublattices making up the structure are slightly different because the two Z numbers are slightly different: 49 and 51. Here is an example of two crystals of very similar crystal structure, one being centrosymmetric, the other one slightly acentric. If the **P**, **H**, and **P**−**H** reflections are strong and of comparable intensities, the three-beam experiment yields azimuthal plots that are practically identical (see Fig. 6). If, on the other hand, the **P** reflection is weak, and the **H** and **P**−**H** reflections are strong, according to the prescriptions of virtual Bragg scattering, the plots of Fig. 7 are obtained, which look quite different.

The asymmetry effect is almost absent in the case of InSb. Furthermore, the little asymmetry visible in the top part of Fig. 7 is reversed with respect to the bottom part. This example clearly shows that the choice of reflections plays a crucial role in detecting small departures from centrosymmetry.

The only other observations of noncentrosymmetric decagonal structures were obtained using convergent-beam electron diffraction,[21,22] where transformations from noncentrosymmetric to centrosymmetric structures were observed as functions of composition. It is surprising that the three quasicrystalline alloys investigated in this work have the same lattice constants, to three significant digits. We are tempted to conclude that the structures are identical, but this is not the case. The relative intensities of the peaks in the

azimuthal plots are quite different. For example, some three-beam peaks are visible in Al-Cu-Co, but not in Al-Ni-Fe or in Al-Ni-Co.[23] This difference becomes dramatic when we compare, for example, the scan in Fig. 4 with that of Fig. 3 (bottom), for which the reflections involved are the same, but the triplet invariants ($\delta = 83°$ and 50°, respectively) are quite different.

The multiple diffraction method is extremely sensitive to very small deviations from centrosymmetry. The issue is discussed in detail in Ref. 5 (Sec. V) where it is shown that a weakly noncentrosymmetric crystal such as GaAs exhibits triplet invariants equal to 90° for certain choices of reflections even when the electron imbalance between Ga and As is vanishingly small.

There is a possibility that, in view of this extreme sensitivity, our results may have been affected by phason strain. For example, if the quasicrystals examined actually consisted of centrosymmetric, overlapping quasicrystalline domains, each domain having a different amount of phason strain, noncentrosymmetric δ values could be seen. However, since phason strain varies greatly with composition and growth conditions, one would expect to see such an effect more strongly pronounced in some materials than in others. To date, the three decagonal compositions mentioned in this work and the two icosahedral samples studied previously[4,5] have all shown noncentrosymmetric δ values, which would imply that if overlapping, centrosymmetric domains exist, they are characteristic of many quasicrystals.

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