

Structural model of orthorhombic Al₃Co

M. Widom, Rob Phillips, J. Zou & A. E. Carlsson

To cite this article: M. Widom, Rob Phillips, J. Zou & A. E. Carlsson (1995) Structural model of orthorhombic Al₃Co, Philosophical Magazine B, 71:3, 397-406, DOI: [10.1080/13642819508239042](https://doi.org/10.1080/13642819508239042)

To link to this article: <https://doi.org/10.1080/13642819508239042>



Published online: 27 Sep 2006.



Submit your article to this journal [↗](#)



Article views: 32



View related articles [↗](#)

Structural model of orthorhombic Al₃Co

By M. WIDOM

Department of Physics, Carnegie–Mellon University, Pittsburgh,
Pennsylvania 15213, USA

ROB PHILLIPS

Division of Engineering, Brown University, Providence,
Rhode Island 02912, USA

J. ZOU

Metals and Ceramics Division, Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831-6115, USA

and A. E. CARLSSON

Department of Physics, Washington University, St Louis,
Missouri 63130-4899, USA

[Received 22 July 1994 and accepted 27 September 1994]

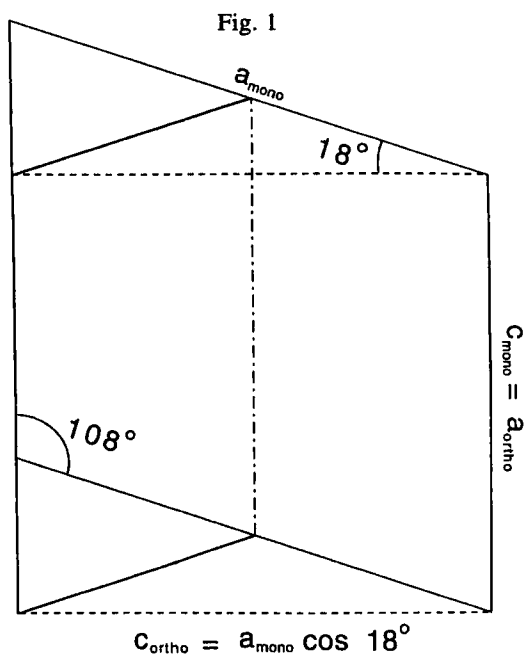
ABSTRACT

The Al–Co alloy system contains a phase Al₃Co of unknown structure. Recently Ma and Kuo determined its space group as *Pn**mn* with lattice constants $a = 12.5 \text{ \AA}$, $b = 8.1 \text{ \AA}$ and $c = 14.6 \text{ \AA}$. We propose a structural model for the orthorhombic phase of Al₃Co including explicit atomic positions and occupancy factors. This model relates to the monoclinic phase of Al₁₃Co₄ by periodic twinning. Our model displays mechanical and thermodynamic stability as determined using approximate pair potentials developed for the Al–Co alloys.

The binary alloy system Al–Co contains several aluminium-rich phases with complex structure including monoclinic Al₉Co₂ with 28 atoms per cell, hexagonal Al₅Co₂ with 22 atoms per cell, and monoclinic Al₁₃Co₄ with 102 atoms per cell. There are also reports (Hudd and Taylor 1962, Goedecke 1971, McAlister 1989) of an additional phase with nominal composition Al₃Co between Al₁₃Co₄ and Al₅Co₂. Using selected-area electron diffraction, Ma and Kuo (1992) identified the space group of this compound as *Pn**mn* and measured the orthorhombic lattice constants $a = 12.5 \text{ \AA}$, $b = 8.1 \text{ \AA}$ and $c = 14.6 \text{ \AA}$. They also noted (fig. 1) a relationship to the lattice constants of monoclinic Al₁₃Co₄ ($a = 15.2 \text{ \AA}$; $b = 8.1 \text{ \AA}$; $c = 12.3 \text{ \AA}$; $\beta = 108^\circ$):

$$\begin{aligned} a_{\text{ortho}} &\approx c_{\text{mono}} \\ b_{\text{ortho}} &\approx b_{\text{mono}} \\ c_{\text{ortho}} &\approx a_{\text{mono}} \cos(\beta - 90^\circ). \end{aligned} \tag{1}$$

We build on their observations to propose an explicit atomic model for the Al₃Co structure. Using electronic-structure-based pair potentials developed for the Al–Co alloy system we examine the energetics of this model. It possesses both mechanical and



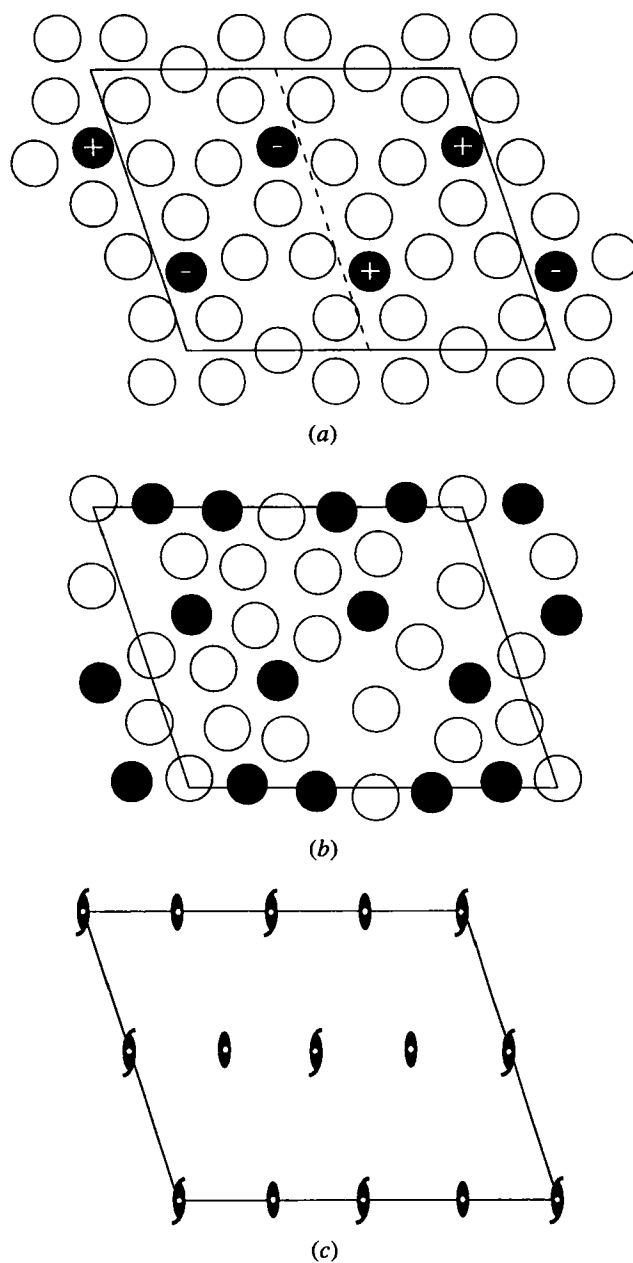
Creation of an orthorhombic cell from two half monoclinic cells. Cut along the chain line to bisect the monoclinic cell. Insertion of glide plane creates a full orthorhombic cell. The orthorhombic *a* axis becomes the monoclinic *c* axis. The broken lines denote the orthorhombic *c* axes.

thermodynamic stability. We also report the calculated atomic positions and occupancy factors.

Decagonal-phase quasicrystals occur frequently in ternary alloys of aluminium, cobalt and either nickel or copper (He, Li and Kuo 1988, Tsai, Inoue and Masumoto 1989, Steurer and Kuo 1990, Hiraga, Lincoln and Sun 1991, Grushko 1993, Fettweis, Launois, Reich, Wittmann and Dénoyer 1994). Depending on details of composition and preparation, layering periodicities of 4, 8, 12, and 16 Å are observed. Structural models for these quasicrystals frequently use crystalline 'approximants' with known structures as templates for local atomic configurations. Approximants (Elser and Henley 1985) are complex crystalline phases close in composition and with a presumed structural similarity to the quasicrystal. Both Al_5Co_2 and especially $\text{Al}_{13}\text{Co}_4$ serve as decagonal-phase approximants with 8 Å layering periodicity. To understand the fundamental building blocks of the quasicrystal structure, it helps to examine as many approximants as possible. Thus the identification of Al_3Co as another 8 Å quasicrystal approximation by Ma and Kuo (1992) motivates us to consider its atomic structure. Slow cooling of binary Al-Co alloys near the composition Al_3Co yields decagonal quasicrystals with the appropriate 8 Å periodicity, further motivating our examinations of the Al_3Co structure.

Figure 2 illustrates the centred-monoclinic structure of $\text{Al}_{13}\text{Co}_4$ in layers perpendicular to the unique *b* axis. Puckered layers (fig. 2 (a)) alternate with flat mirror planes (fig. 2 (b)) in the sequence FPF'P'. The puckered layers P and P' are reflections of each other through the intervening flat layer; so their horizontal projections are identical. The flat layer F' is obtained from F by translation through $\frac{1}{2}\mathbf{a}$. The solid lines in figs. 2 (a) and (b) outline one unit cell. Although rigorously the symmetry of $\text{Al}_{13}\text{Co}_4$

Fig. 2



Structure of monoclinic $Al_{13}Co_4$ showing sections perpendicular to the b axis. Lines bound unit cells. The open circles represent aluminium while the full circles represent cobalt atoms. (a) Puckered P layer. (b) Flat F layer. The broken line in P runs along the pseudo-glide plane. The + and - signs on cobalts denote vertical displacements. (c) Symmetry elements of $C2/m$. The spirals are 2_1 screw axes with inversion. The ovals are twofold rotations with inversion.

is Cm , minute atomic displacements raise its symmetry to the $C2/m$ symmetry of $Al_{13}Fe_4$. The following discussion assumes $C2/m$ symmetry and fig. 2 (c) illustrates the symmetry elements of this higher-symmetry group.

Figure 3 shows our proposed orthorhombic structure. It obeys the relationship between the orthorhombic and monoclinic unit cell lattice constants observed by Ma and Kuo and illustrated in fig. 1. We achieve this relationship between the lattice constants while imposing the observed $Pnmm$ space group by the following construction: take one half of a monoclinic cell, cut in the $\mathbf{b-c}$ plane, for use as a half orthorhombic cell. To find the other half orthorhombic cell simply apply a diagonal glide reflection (an n glide). This means translate by $\frac{1}{2}(\mathbf{b} + \mathbf{c})$ and then reflect through the $\mathbf{b-c}$ plane. Joining the two monoclinic half-cells produces the full orthorhombic cell. We explicitly insert just one diagonal glide. The presence of a twofold symmetry axis parallel to the glide plane, but not contained within it, then guarantees the full set of four glide planes evident in fig. 3 (c).

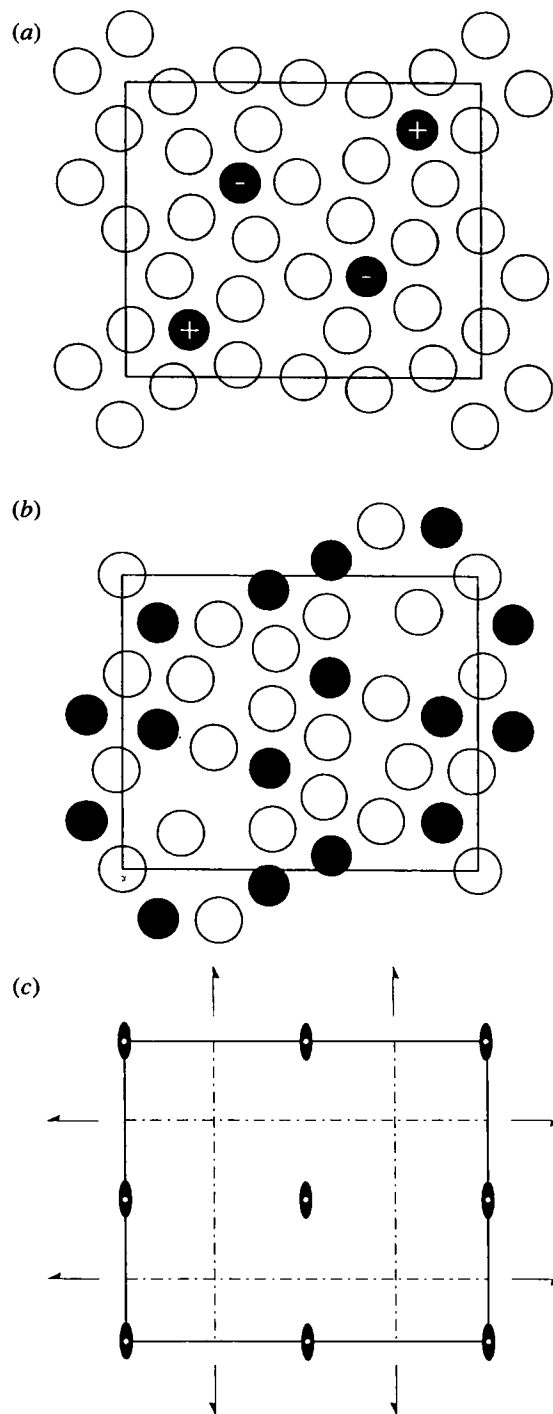
Placement of the cut within the monoclinic unit cell strongly influences the orthorhombic energy. To achieve low energy, we require that the local atomic arrangements in the new orthorhombic $Pnmm$ structure resemble local atomic arrangements in the earlier monoclinic $C2/m$ structure. For example, the twofold symmetry axes of the monoclinic phase become the twofold symmetry axes of the new orthorhombic structure. The glide plane, where two half monoclinic cells are glued to form the orthorhombic cell, could suffer arbitrarily large energy costs from disadvantageous interatomic spacings across the plane. We show now that the monoclinic structure possesses a pseudo-diagonal-glide plane; so interatomic spacings within a distance of 3.5 Å on either side of the cut remain essentially unchanged after orthorhombic symmetry is imposed.

Examine the puckered layer P of the monoclinic structure in fig. 2 (a). One of the rows of twofold screw axes is highlighted with a broken line. Out to a distance of 3.5 Å on each side of these rows the structure exhibits a glide plane along $\frac{1}{2}\mathbf{c}$. When displacements in the vertical direction are considered (see the + and - signs on the cobalt atoms in fig. 2 (a)) it is apparent that vertical displacements of P and P' have been interchanged. Adding a $\frac{1}{2}\mathbf{b}$ translation restores symmetry while converting the c glide into a diagonal glide. The same is true for the flat layers. To see this by inspection of fig. 2 (b), recall that F and F' differ by a $\frac{1}{2}\mathbf{a}$ translation. Thus the monoclinic structure contains a pseudo-diagonal-glide plane. We therefore expect the energy of the orthorhombic structure to be very close to the monoclinic energy.

Some structural models for decagonal quasicrystals and approximants use geometrical tiles as a short-hand for actual atomic positions. In fig. 4 we show such a tiling decomposition of the monoclinic and orthorhombic structures. The puckered layers consist of pentagon-rectangle-triangle tilings while the flat layers contain pentagons and rhombuses. The similarity of the tilings is another indication that monoclinic and orthorhombic structures should be close in energy. Similar motifs describe Al_5Co_2 and Al_3Mn (Li, Shi and Kuo 1992, Hiraga, Kaneko, Matsuo and Hashimoto 1993). We believe that our proposed orthorhombic structure is the only arrangement of such motifs with $Pnmm$ symmetry and the required lattice constants. The rearrangement from monoclinic to orthorhombic is presumably related to phasons in the associated quasicrystal phase. An alternate structural description is possible in terms of Henley's (1993) pentagonal bipyramids.

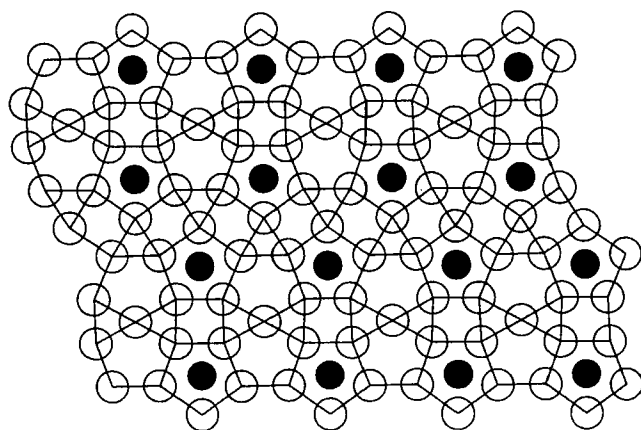
To examine the energetic stability of this proposed structure we define the total energy as a sum over all atom pairs using pair potentials derived for aluminium-rich

Fig. 3

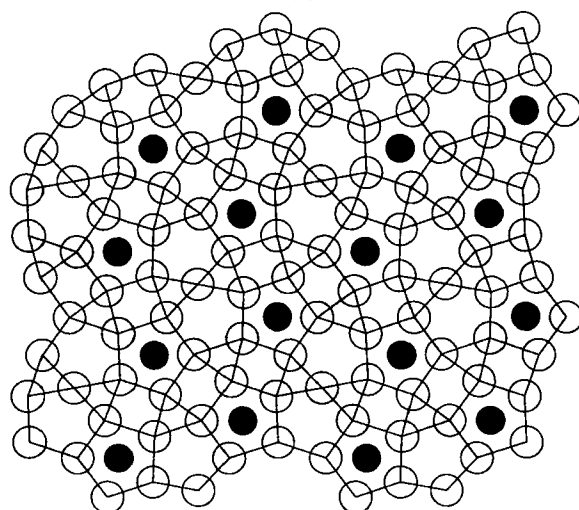


Proposed structure of orthorhombic Al_3Co_4 . The horizontal axis is c , and the vertical axis is a . (a) Puckered layer P. The + and - signs on cobalt atoms denote vertical displacements. (b) Flat layer F. (c) Symmetry elements of $Pmmn$. The ovals are twofold rotations with inversion. The chain lines are diagonal glides.

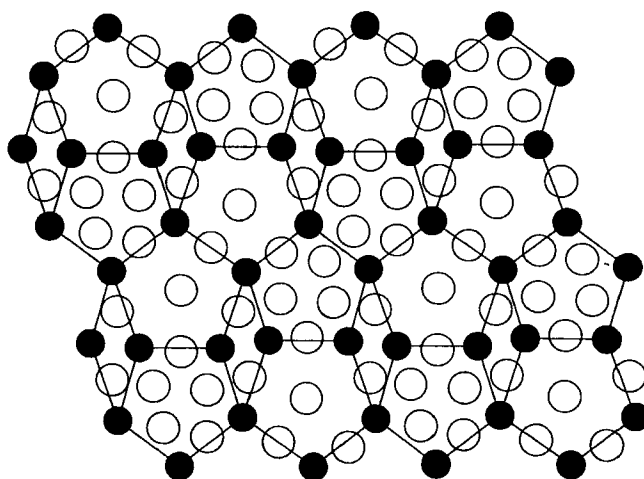
Fig. 4



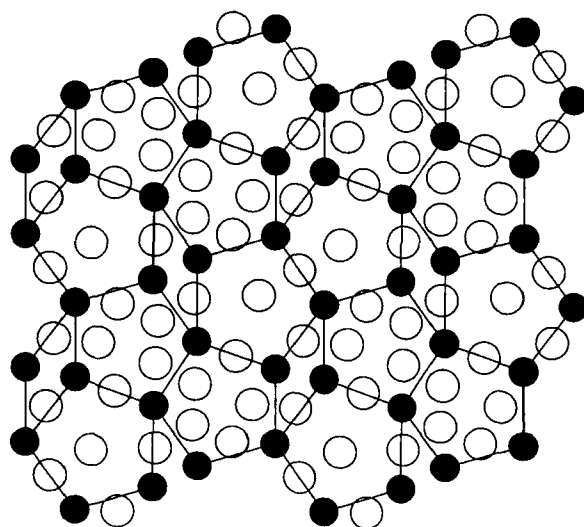
(a)



(b)



(c)



(d)

(a) Tiling of monoclinic puckered layer by pentagons, rectangles, and triangles. (b) Same for orthorhombic. (c) Tiling of monoclinic flat layer by pentagons and rhombuses. (d) Same for orthorhombic.

Wyckoff coordinates for orthorhombic Al₃Co (space group, No. 58, *Pnmm*; lattice constants $a = 12.5 \text{ \AA}$, $b = 8.1 \text{ \AA}$ and $c = 14.6 \text{ \AA}$).

| Atom | Wyckoff site | Symmetry | x | y | z | Occupancy |
|--------|--------------|----------|-------|-------|-------|-------------------|
| Al(1) | 4f | 2 | 0.500 | 0.250 | 0.000 | 1.00 |
| Al(2) | 8h | 1 | 0.237 | 0.272 | 0.179 | 1.00 |
| Al(3) | 8h | 1 | 0.033 | 0.226 | 0.135 | 1.00 |
| Al(4) | 8h | 1 | 0.159 | 0.277 | 0.375 | 1.00 |
| Al(5) | 8h | 1 | 0.340 | 0.278 | 0.484 | 1.00 |
| Al(6) | 8h | 1 | 0.460 | 0.278 | 0.186 | 1.00 |
| Co(1) | 8h | 1 | 0.342 | 0.196 | 0.321 | 1.00 |
| Al(7) | 2a | 2/m | 0.000 | 0.000 | 0.000 | 1.00 |
| Al(8) | 4g | m | 0.339 | 0.000 | 0.016 | 1.00 |
| Al(9) | 4g | m | 0.451 | 0.000 | 0.421 | 1.00 |
| Al(10) | 4g | m | 0.169 | 0.000 | 0.271 | 0.15 |
| Al(11) | 4g | m | 0.585 | 0.000 | 0.257 | 0.05 |
| Al(12) | 4g | m | 0.140 | 0.000 | 0.577 | 1.00 |
| Al(13) | 4g | m | 0.250 | 0.000 | 0.431 | 0.90 Al + 0.10 Co |
| Al(14) | 4g | m | 0.355 | 0.000 | 0.191 | 1.00 |
| Al(15) | 4g | m | 0.125 | 0.000 | 0.835 | 0.10 |
| Co(2) | 4g | m | 0.523 | 0.000 | 0.098 | 1.00 |
| Co(3) | 4g | m | 0.654 | 0.000 | 0.413 | 1.00 |
| Co(4) | 4g | m | 0.052 | 0.000 | 0.410 | 1.00 |
| Co(5) | 4g | m | 0.164 | 0.000 | 0.100 | 1.00 |

cobalt alloys (Phillips, Zou, Carlsson and Widom 1994). Upon relaxing atomic positions to minimize the energy, atomic displacements were small (mean displacement of 0.21 Å), implying mechanical stability of the structure. The table lists the coordinates after relaxation. The resulting energy was 0.080 eV atom⁻¹ while a similar calculation for the monoclinic structure produced energy 0.076 eV atom⁻¹. Thus at the composition Al₇₈Co₂₄, the monoclinic structure is favoured over the orthorhombic.

Ma and Kuo suggest the composition Al₁₁Co₄ for the orthorhombic phase. To identify sites for aluminium vacancies, we performed a Monte Carlo simulation in which 66 aluminium and 24 cobalt atoms were distributed among the sites listed in the table. Each site could be vacant or occupied by aluminium or by cobalt. The resulting occupation probabilities (at 500 K) are listed in the table. We see that the vacancies lie entirely within the flat mirror planes on three different Wyckoff sites of multiplicity 4. Removing these 12 low-occupancy sites and relaxing again results in mean atomic displacements of 0.25 Å and energy - 0.030 eV atom⁻¹. A similar calculation for the monoclinic structure produced an energy of - 0.004 eV atom⁻¹, implying that a low aluminium concentration favours the orthorhombic structure. This result is consistent with the observed phase diagram where the orthorhombic phase lies farther from pure aluminium than does the monoclinic phase. At the composition Al₆₆Co₂₄ the energy of the orthorhombic structure is 0.056 eV atom⁻¹ below the tie-line connecting relaxed monoclinic Al₇₈Co₂₄ with relaxed Al₅Co₂. Thus our calculation shows that the orthorhombic structure enjoys not only mechanical stability (from small displacements under relaxation) but also thermodynamic stability against phase separation into other known crystal phases.

Insertion of a single glide plane into the monoclinic structure creates a mixed stacking-fault-twin boundary which we call a diagonal-glide boundary defect. (Black (1955)) discusses this defect in the context of twinning in Al₃Fe). Similarly, the insertion of screw axes with inversion in place of orthorhombic glide planes creates an inversion boundary defect. To calculate these defect energies, we recognize that each unit cell contains two walls of area 8.1 Å × 12.34 Å spaced by 7.3 Å. The defect energy is

$$E_d = \frac{\Delta E}{2 \times 8.1 \times 12.3} \text{ eV } \text{Å}^{-2}, \quad (2)$$

where ΔE is the energy difference per unit cell between monoclinic and orthorhombic structures. The defect energy thus calculated represents a combination of the energy to create a single defect and the interaction energy of two defects spaced 7.3 Å apart. Substituting our calculated ΔE values we obtain $E_i = 0.002 \text{ eV/Å}^{-2}$ for diagonal-glide defects in monoclinic Al₇₈Co₂₄ and $E_d = 0.012 \text{ eV } \text{Å}^{-2}$ for inversion boundaries in orthorhombic Al₆₆Co₂₄. These defect energies are in line with defect wall energies in many metals and alloys. Furthermore, ΔE for each type of defect reverses sign between these two compositions. Thus, at the composition Al₆₆Co₂₄, it is energetically favourable to insert diagonal-glide defects into the monoclinic structure. Repeated diagonal-glide defects every half-unit cell along the **a** axis convert monoclinic Al-Co into orthorhombic Al-Co. Similarly, at the composition Al₇₈Co₂₄, it is favourable to insert repeated inversion boundaries into the orthorhombic structure spaced every half-unit cell along the **c** axis which convert orthorhombic Al-Co back into monoclinic Al-Co.

Electron microscopy can image isolated wall defects, and electron diffraction can reveal the consequent streaking in the diffraction patterns. In the monoclinic crystal, the streaking should run parallel to the **a*** reciprocal space axis. In the orthorhombic

crystal, streaking should run parallel to c^* . It would be of great interest to image these defects and to see whether they proliferate at compositions between the preferred compositions of monoclinic and orthorhombic Al–Co.

Note that we include no error estimates on our calculated values of energies, coordinates and occupations. Systematic errors of unknown magnitude arise from

- (a) our pair potential approximation,
- (b) neglect of electron density variation upon compositional change,
- (c) coordinates given for an ideal composition not the true composition and
- (d) atomic vibrations neglected in calculating occupation probabilities.

Thus our proposed structure may provide a satisfactory starting point but not a substitute for precise experimental determinations.

In conclusion, we propose an explicit structure for the orthorhombic phase Al_3Co . Approximate pair potentials for aluminium–cobalt alloys predict this structure to be stable and to be between monoclinic $Al_{13}Co_4$ and hexagonal Al_5Co_2 , consistent with the known phase diagram. Experimental tests of our model include the structure determination of orthorhombic Al_3Co and identification of wall defects in both the orthorhombic and the monoclinic variants. Verification of this model will support the notion of quasicrystal structure as a rearrangement of structural motifs inherited from conventional crystals.

NOTE ADDED DURING REVIEW

We recently learned of two experimental studies which generally confirm our proposed structure. One, by Li, Ma and Kuo (1994), employs high-resolution electron microscopy and relates the orthorhombic structure to the monoclinic one through repeated (100) faults. Except for a shift in origin and swapping of a and c axes, the resulting structure differs from ours only by small atomic displacements which average 0.1 Å for cobalt atoms and 0.2 Å for fully occupied aluminium sites but reach 0.5 Å for our low-occupancy aluminium sites. The other, by Grin, Burkhardt, Ellner and Peters (1994), employs single-crystal X-ray diffraction. This study suggests the space group $Pnm2_1$ (a subgroup of $Pmnm$) and fully atomic occupancy $Al_{78}Co_{24}$ for the orthorhombic phase. They do not observe the monoclinic phase in binary Al–Co alloys. Again, the atomic positions agree with ours except for slight deviations. We have relaxed the structure obtained by Grin *et al.* at both full and partial occupancy. Our results suggest the lower symmetry $Pnm2_1$ may be more stable than the higher symmetry $Pmnm$ at full occupancy (but still not as stable as the monoclinic structure), while the higher $Pmnm$ symmetry appears to be preferred for partial aluminium occupancy. We are indebted to Dr Kuo and Dr Grushko for bringing these references to our attention.

ACKNOWLEDGMENTS

We are grateful to P. Launois for bringing the paper by Ma and Kuo (1992) to our attention. M. McHenry and M. de Graef offered useful comments on defects. We owe thanks to Serdar Ogut and Karin Rabe for supplying us with *ab-initio* results on structural energy differences used in creating our pair potentials. This work was supported by the US Department of Energy under Grant No. DE-FG02-84ER45130 at Washington University and Grant No. DE-FG02-89ER45405 at Cornell University and by National Science Foundation Grant No. DMR-9221596 at Carnegie Mellon University. Work at Oak Ridge National Laboratory is sponsored by the Division

of Materials Sciences, US Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES

- BLACK, P. J., 1955, *Acta crystallogr.*, **8**, 43, 175.
ELSER, V., and HENLEY, C. L., 1985, *Phys. Rev. Lett.*, **55**, 2883.
FETTWEIS, M., LAUNOIS, P., REICH, R., WITTMANN, R., and DÉNOYER, F., 1994, *Phys. Rev. Lett.* (submitted).
GOEDECKE, T. (1971), *Z. Metallkd.*, **62**, 842.
GRIN, J., BURKHARDT, U., ELLNER, M., and PETERS, K., 1994, *J. Alloys Compounds*, **206**, 243.
GRUSHKO, B., 1993, *J. non-crystalline Solids*, **153–154**, 489.
HE, L. X., LI, X. Z., and KUO, K. H., 1988, *Phys. Rev. Lett.*, **61**, 1116.
HENLEY, C. L., 1993, *J. non-crystalline Solids*, **153–154**, 172.
HIRAGA, K., KANEKO, M., MATSUO, Y., and HASHIMOTO, S., 1993, *Phil. Mag. B*, **67**, 193.
HIRAGA, K., LINCOLN, F. J., and SUN, W., 1991, *Mater. Trans. Japan Inst. Metals*, **32**, 308.
HUDD, R. C., and TAYLOR, W. H., 1962, *Acta crystallogr.*, **15**, 441.
LI, X. Z., SHI, D., and KUO, K. H., 1992, *Phil. Mag. B*, **66**, 331.
LI, X. Z., MA, X. L., and KUO, K. H., 1994, *Phil. Mag. Lett.*, **70**, 221.
MA, X. L., and KUO, K. H., 1992, *Metall. Trans. A*, **23**, 1121.
MCALISTER, A. J., 1989, *Bull. Alloy Phase Diagrams*, **10**, 646.
PHILLIPS, R., ZOU, J., CARLSSON, A. E., and WIDOM, M., 1994, *Phys. Rev. B*, **49**, 9322.
STEURER, W., and KUO, K. H., 1990, *Acta crystallogr. B*, **46**, 703.
 TSAI, A. P., INOUE, A., and MASUMOTO, T., 1989, *Mater. Trans. Japan Inst. Metals*, **30**, 463.