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On the ordered structure proposed for Li_3Mg_5.*

By F. H. Herbstein and B. L. Averbach, *Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A.*

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Berry & Raynor (1953) have recently reported that a transitional ordered structure is formed at the ideal composition Li_3Mg_5 in the presence of interstitial contaminants (oxygen and nitrogen). This transitional structure was found on one occasion accompanying the normal disordered body-centered cubic phase in small amounts, the evidence being the presence of nineteen faint lines, in addition to those of the body-centered cubic cell, on a powder photograph of an alloy with 34 atomic % Li. These extra lines were indexed in terms of a cubic cell with $a_0 \simeq 9{\cdot}7$ Å, the arrangement of the atoms being that shown in Fig. 1. The lattice spacing of the proposed structure is approximately $2\sqrt{2}.a$, where a is the lattice parameter of the β-phase alloy, and it was suggested that 'the new structure may be regarded as formed by an expansion of the [001] direction in the (body-centered) cubic structure by a factor of $\sqrt{2}$, accompanied by ordering'. We have recently attempted to reproduce the ordered structure, Li_3Mg_5, but without success. Detailed examination of the structure proposed by Berry & Raynor shows that it is unlikely to be formed unless it contains almost as many interstitial as metal atoms.

An immediate objection to the proposed structure is that its symmetry is not cubic, as Berry & Raynor stated, but tetragonal. This may be seen at once from the fact that the a_1 and a_2 axes in Fig. 1 are interchangeable with each other, but not with a_3. The cell originally proposed is not the simplest unit cell, and a simpler cell, also tetragonal, is shown in Fig. 1. The space group of the structure is now $I4/m$–C^5_{4h} (No. 87 of *International Tables* (1952)) and the atoms lie at the following special positions:

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})+$$

2 Mg in (a): $(0, 0, 0)$;
8 Mg in (f): $(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}), (\tfrac{3}{4}, \tfrac{1}{4}, \tfrac{1}{4}), (\tfrac{1}{4}, \tfrac{3}{4}, \tfrac{1}{4}), (\tfrac{3}{4}, \tfrac{3}{4}, \tfrac{1}{4})$;
2 Li in (b): $(0, 0, \tfrac{1}{2})$;
4 Li in (c): $(\tfrac{1}{2}, 0, 0), (0, \tfrac{1}{2}, 0)$.

In the new tetragonal cell the lattice dimensions must have $c/a = \sqrt{2}$ in order to maintain the pseudo-cubic symmetry of the powder pattern observed by Berry & Raynor. It must, however, be accounted fortuitous that the axial ratio is exactly $\sqrt{2}$, and some splitting of the powder lines would be expected.

A second, and more serious, objection to the structure of Fig. 1 is based on a consideration of the nearest-neighbor interatomic distance, which is 3·5 Å in the proposed structure but averages only 3·03 Å in the disordered body-centered cubic cell. Thus the postulated transformation would be accompanied by an increase of about one-third in the mean volume per atom. This is in contrast to a normal ordering transformation, where the volume change is about 1% or less, and suggests at once that the uncontaminated structure of Fig. 1 will not be stable.

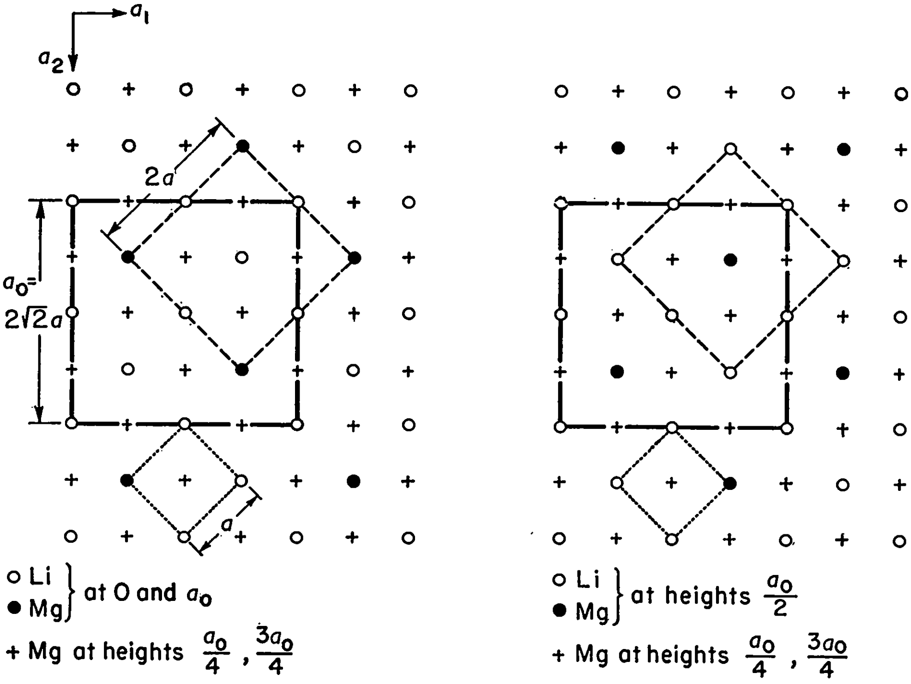

Fig. 1. The arrangement of the atoms in the Li_3Mg_5 structure proposed by Berry & Raynor. The pseudo-cubic unit cell used by these authors is outlined in full lines; the simpler tetragonal cell used in the present discussion is outlined in broken lines and the original body-centered cubic cell in dotted lines. The coordinate system shown applies only to the Berry–Raynor cell.

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Table 1. *Expressions for the structure factors of the unstabilized* Li_3Mg_5 *and the stabilized structure containing interstitial atoms*

(f_I is the atomic scattering factor of the interstitial atom)

Conditions on reflection indices	Unstabilized structure (metal atoms only)	Stabilized structure (metal+interstitial atoms)
$h+k+l \neq 2n$	0	0
$h+k+l = 2n$	—	—
(1) h, k, l mixed	$2(f_{Mg}-f_{Li})$	$2(f_{Mg}-f_{Li})$
(2) h, k, l all even	—	—
(*a*) $\frac{1}{2}(h+k+l)$ odd	$6(f_{Li}-f_{Mg})$	$6(f_{Li}-f_{Mg})$
(*b*) $\frac{1}{2}(h+k+l)$ even, $\frac{1}{2}l$ even	$6f_{Li}+10f_{Mg}$	$6f_{Li}+10f_{Mg}+16f_I$
$\frac{1}{2}(h+k+l)$ even, $\frac{1}{2}l$ odd	$6f_{Li}+10f_{Mg}$	$6f_{Li}+10f_{Mg}-16f_I$

It is possible to produce the necessary expansion of the original lattice in the [001] direction by a suitable arrangement of interstitial atoms, but the powder pattern from this stabilized structure differs significantly from that due to the unstabilized structure. The expansion of the [001] direction can be produced by introducing interstitial atoms into the octahedral sites at $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$ and symmetry-related positions of the original body-centered cubic cell. In terms of the new cell these positions are:

$(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$
4 interstitials in (*d*): $(0, \frac{1}{2}, \frac{1}{4})$;
4 interstitials in (*e*): $(0, 0, z)$ with $z = \frac{1}{4}$;
8 interstitials in (*h*): $(x, y, 0)$, $(\bar{y}, x, 0)$, $(y, \bar{x}, 0)$, $(\bar{x}, \bar{y}, 0)$ with $x = y = \frac{1}{4}$.

If the interstitial atoms are oxygen, then filling of all sixteen sites would increase the [001] dimension from 2×3·5 Å to 9·9 Å, close to the observed 9·7 Å; with nitrogen atoms it would be sufficient to fill only three-quarters of these sites to expand the lattice sufficiently. Again it must be considered highly fortuitous that this expansion is such as to make c/a exactly equal to $\sqrt{2}$.

The expressions for the structure factors of the unstabilized structure of Fig. 1 and that stabilized by sixteen interstitial atoms are given in Table 1. There are five groups of reflections, out of eighteen between Bragg angles for Cu $K\alpha$ of 8° and 32°, for which structure factors differ significantly; these are the reflections 202; (220, 004); (400, 224); (422, 206) and 044. The bracketed reflections overlap for $c/a = \sqrt{2}$. The interstitial atoms do not contribute to the superstructure reflections, which are therefore the same in both structures.

We have already noted that the uncontaminated structure of Fig. 1 appears to be improbable because of the volume change that would be involved in its formation. This volume change can be accounted for by adding to the unit cell a number of interstitial atoms approximately equal to the number of metal atoms present. The values of the structure factors for the two cells suggest that it would not be too difficult to confuse their powder patterns, especially if quantitative intensity measurements were not made. We conclude that it is improbable that uncontaminated alloys of composition Li_3Mg_5 could have the structure of Fig. 1; the stabilized structure, which cannot be termed an alloy of Li and Mg, is a possible explanation for the observed powder pattern, but its existence must remain essentially speculative until confirmed by density measurements or accurate intensity measurements.

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Refinement of the P–P bond length in P_4S_7.

By Aafje Vos and E. H. Wiebenga, *Laboratorium voor Anorganische en Fysische Chemie der Rijksuniversiteit Groningen, Netherlands*

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In a recent structure determination of P_4S_7 a remarkably large value, 2·37 Å, for the P–P bond length in the molecule was observed (Vos & Wiebenga, 1955). To this bond length, however, a rather large standard deviation, 0·04 Å, had to be assigned because of overlap in the projections from which the coordinates were derived. It therefore seemed desirable to determine the positions of the two phosphorus atoms concerned (P_1 and P_2) more accurately.

A more reliable value for the P–P bond length has now been obtained by computing the three-dimensional electron-density distribution around P_1 and P_2. The required intensities of the reflexions *hkl* could be taken from the original structure determination in which they had been used for the calculation of a three-dimensional Patterson synthesis. The scale and temperature factors were redetermined separately for the different layer lines by comparison with the calculated structure factors. The disagreement index R amounted to 0·13; the best average value for the temperature factor was $\exp(-2{\cdot}8\sin^2\theta/\lambda^2)$, which is slightly different from the value obtained during the two-dimensional refinement.

For locating the peak maxima an analytical method (Shoemaker, Donohue, Schomaker & Corey, 1950) was used; a back-shift correction for series termination was applied. The results are shown in Table 1. Since the