Lattice Constants and Brillouin Zone Overlap in Dilute Magnesium Alloys

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The lattice constants of primary solid solutions of indium, aluminum, and cadmium in magnesium have been determined as a function of composition. A sharp change in (c/a) has been found only for magnesium-indium. The linearity of the (c/a) vs concentration curve for magnesium-aluminum has suggested that electron zone overlap does not necessarily lead to axial ratio anomalies and that changes in short-range order may be needed to explain such anomalies.

I. INTRODUCTION

IN a number of papers on the variation of the lattice constants of magnesium on alloying, there has been an increasing acceptance of the idea that the variation of the axial ratio is determined primarily by the electronic concentration of the alloy and not by atomic concentration or other purely atomic properties. This idea is due largely to the experimental work of Hume-Rothery and Raynor[1] and Raynor,[2] who made accurate measurements of the variation of the lattice constants of magnesium with the addition of various solute metals. They found that indium and aluminum additions caused a sharp change in the (c/a) vs composition curve at about 0.75 atomic percent, and that tin and lead additions caused a break at somewhat lower concentrations, while for cadmium and silver additions no such break was apparent. This sort of evidence seemed to indicate that the presence and position of the break was determined by the valency of the solute.

Jones[3,4] has given simple theoretical treatments of the problem in which he has calculated the variation of (c/a) as a function of electronic additions, based on a Brillouin zone model. In this model the addition of trivalent and quadrivalent solutes to magnesium results in an expansion of the Fermi surface and a resulting overlap at the second Brillouin zone boundary in the (001) direction. This gives rise to a sharp change in the axial ratio at the electron concentration where overlap occurs.

Salkovitz and Schindler[5] have recently initiated an extensive study of the electronic properties of dilute magnesium alloys. They have measured the Hall constant,[6] the thermal coefficient of resistivity,[7] and with Kammer the thermoelectric power[8] for a number of dilute magnesium alloys including those of indium and aluminum. They have interpreted their measurements[7] as indicating zone overlap occurring between 1.5 and 2.3 atomic percent in the magnesium-indium system and between 1.0 and 1.3 atomic percent in magnesium-aluminum.

These regions of overlap differ considerably from the concentration at which Hume-Rothery and Raynor found breaks in their lattice parameter measurements.

The present work was undertaken, partly to find out whether the break in (c/a) vs composition as determined on the same samples that were used for the measurements of the electronic properties would reveal a better agreement with those measurements. In addition, since the number of alloys in the critical concentration region was larger than those available to Raynor, it was hoped that more detailed information on the shape of the curve in the region of the break would be obtained. It was also hoped that these measurements would permit an evaluation of the assumption that the observed breaks are functions of the electronic concentration alone.

II. LATTICE CONSTANT DETERMINATION

The dilute magnesium alloys of indium, cadmium, and aluminum used in the investigations of Schindler and Salkovitz and of Kammer were used to obtain precision lattice constants at room temperature (25°C). These alloys were originally obtained from the Dow Chemical Company with an accurate analysis of the alloying element present. Filings for x-ray analysis were obtained by filing the alloys in a dry box, which was evacuated, filled with purified argon, re-evacuated and refilled with purified argon. The filings were placed in quartz tubes which were sealed under vacuum, annealed at 310°C for 16 hours and quenched in water. The tubes were then broken and the filings screened with a 325-mesh sieve. The lattice constants were determined from diffraction patterns made with a back-reflection symmetric parafocusing camera with iron (Fe) radiation (Fe $K\alpha_1 = 1.93597$ A; Fe $K\alpha_2 = 1.93991$ A) using Jette and Foote's[9] modification of Cohen's method.

[1] Hume-Rothery and G. V. Raynor, Proc. Roy. Soc. (London) **177**, 27 (1940-1941).
[2] G. V. Raynor, Proc. Roy. Soc. (London) A174, 447 (1940); and A180, 107 (1942).
[3] H. Jones, Proc. Roy. Soc. (London) A147, 400 (1934).
[4] H. Jones, Phil. Mag. 41, 633 (1950).
[5] E. I. Salkovitz and A. I. Schindler, Phys. Rev. **91**, 234(A) (1953).
[6] A. I. Schindler and E. I. Salkovitz, Phys. Rev. **91**, 1320 (1953); Phys. Rev. **98**, 1552(A) (1955).
[7] E. I. Salkovitz and A. I. Schindler (private communication).
[8] Kammer, Salkovitz, and Schindler, Phys. Rev. **100**, 1257(A) (1955).
[9] E. R. Jette and P. D. Foote, J. Chem. Phys. 3, 605 (1935).

TABLE I. Lattice spacings for magnesium alloy systems in angstrom units. All values are at 25°C.

System	Atomic percent solute	a_0 spacing in A at 25°C	c_0 spacing in A at 25°C	Axial ratio c/a	Volume unit cell
Pure Mg (Dow)		$3.2095_6 \pm 0.0002_7$	$5.2107_1 \pm 0.0002_4$	1.6235_0	46.4858
Pure Mg (N.J.Z.)		$3.2093_8 \pm 0.0001_0$	$5.2106_9 \pm 0.0000_9$	1.6235_8	46.4807
Mg-Al	0.29	$3.2085_4 \pm 0.0001_2$	$5.2094_1 \pm 0.0001_1$	1.6236_1	46.4448
	0.52	$3.2072_9 \pm 0.0001_4$	$5.2081_1 \pm 0.0001_2$	1.6238_4	46.3968
	0.80	$3.2062_6 \pm 0.0001_7$	$5.2066_3 \pm 0.0001_5$	1.6238_9	46.3540
	0.88	$3.2059_2 \pm 0.0001_7$	$5.2060_6 \pm 0.0001_5$	1.6238_9	46.3389
	1.31	$3.2045_5 \pm 0.0001_7$	$5.2039_1 \pm 0.0001_5$	1.6239_1	46.2805
	1.64	$3.2030_6 \pm 0.0001_8$	$5.2021_6 \pm 0.0001_6$	1.6241_2	46.2219
	1.82	$3.2021_0 \pm 0.0002_2$	$5.2009_6 \pm 0.0002_0$	1.6242_3	46.1836
	2.18	$3.2011_4 \pm 0.0001_3$	$5.1994_1 \pm 0.0001_1$	1.6242_4	46.1419
	2.40	$3.2003_7 \pm 0.0001_4$	$5.1979_5 \pm 0.0001_3$	1.6241_7	46.1068
Mg-Cd	0.549	$3.2082_4 \pm 0.0002_0$	$5.2088_9 \pm 0.0001_8$	1.6236_0	46.4314
	1.011	$3.2072_6 \pm 0.0001_1$	$5.2074_9 \pm 0.0000_9$	1.6236_6	46.3906
	1.921	$3.2054_3 \pm 0.0001_4$	$5.2045_3 \pm 0.0001_2$	1.6236_7	46.3110
	3.925	$3.2009_4 \pm 0.0001_6$	$5.1983_2 \pm 0.0001_5$	1.6240_0	46.1266
	8.644	$3.1904_2 \pm 0.0001_7$	$5.1827_0 \pm 0.0001_6$	1.6244_6	45.6860
Mg-In	0.446	$3.2089_0 \pm 0.0003_3$	$5.2107_2 \pm 0.0002_9$	1.6238_3	46.4668
	0.862	$3.2083_4 \pm 0.0001_7$	$5.2106_1 \pm 0.0001_5$	1.6240_8	46.4498
	1.457	$3.2077_9 \pm 0.0001_1$	$5.2103_0 \pm 0.0001_0$	1.6242_6	46.4308
	2.300	$3.2071_3 \pm 0.0001_5$	$5.2103_8 \pm 0.0001_3$	1.6246_2	46.4126
	3.008	$3.2060_5 \pm 0.0001_6$	$5.2105_0 \pm 0.0001_4$	1.6252_1	46.3823
	3.74	$3.2053_2 \pm 0.0001_4$	$5.2106_2 \pm 0.0001_3$	1.6256_2	46.3623
	6.76	$3.2016_0 \pm 0.0000_7$	$5.2116_0 \pm 0.0000_6$	1.6278_1	46.2650
	10.57	$3.1962_0 \pm 0.0001_1$	$5.2146_1 \pm 0.0001_1$	1.6315_0	46.1342

The results of the lattice constant determination are tabulated in Table I, together with the unit cell volumes. The errors listed are the 95% confidence limits similar to those used by Jette and Foote.[9] These data are presented graphically in Figs. 1, 2, 3, and 4.

III. DISCUSSION

An examination of Figs. 1 through 4 shows that only in the magnesium-indium system are the deviations from linearity significant. Indeed the points for the other systems can be fitted (by least squares) to straight lines with an exterior standard deviation roughly equal to the precision of the measured points. In addition, the standard deviation for the magnesium-aluminum points are not significantly different from those for the magnesium-cadmium points. Thus, Jones' model in which indium and aluminum should behave similarly does not explain the data. Indeed McClure[10] has shown that local distortions are probably necessary to explain observed departures from linearity
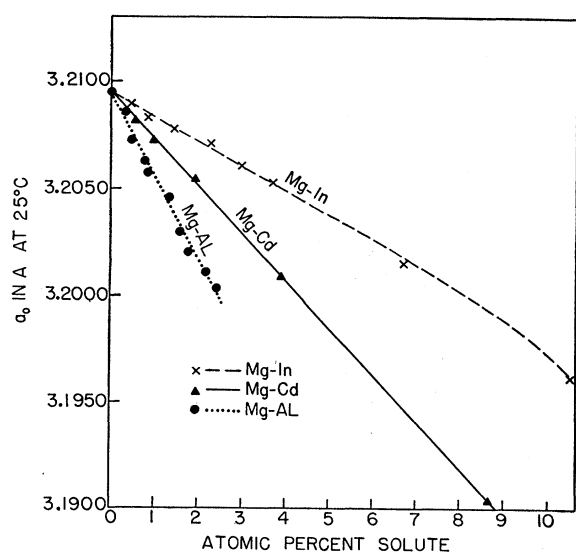

FIG. 1. Lattice constant a_0 (in angstroms) of primary solid solutions of indium, cadmium, and aluminum in magnesium vs atomic percent of solute.
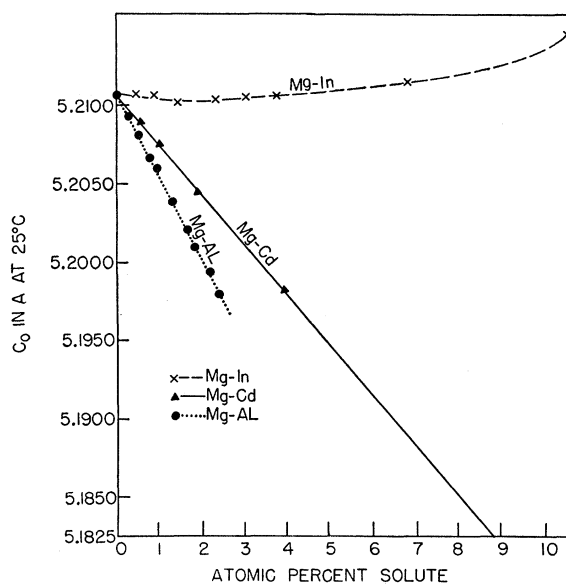

FIG. 2. Lattice constant c_0 (in angstroms) of primary solid solutions of indium, cadmium, and aluminum in magnesium vs atomic percent of solute.

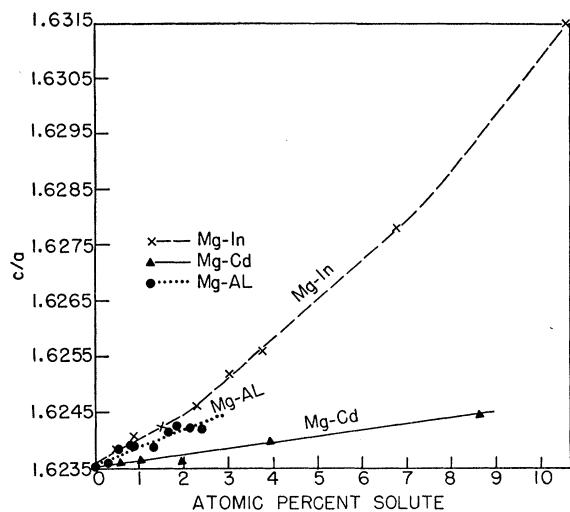[10] J. W. McClure, Phys. Rev. 98, 449 (1955).

FIG. 3. Axial ratio (c/a) of primary solid solutions of indium, cadmium, and aluminum in magnesium vs atomic percent of solute.

FIG. 4. Unit cell volume (in cubic angstroms) of primary solid solutions of indium, cadmium, and aluminum in magnesium vs atomic percent of solute.

in the axial ratio composition plots of dilute magnesium alloys.

The measurement of the electronic properties mentioned earlier seem to give a more positive indication of Brillouin zone overlap than do the present lattice constant data. The rough agreement, for the magnesium-indium system, between the position of the break in the electronic properties and that in the lattice constants may lend credence to the belief that the breaks have a common origin. Yet if they do, one must explain the absence of a significant deviation in the magnesium-aluminum lattice constant data. Thus, for the present at least, the validity of the zone overlap approach must rest primarily upon measurements of the electronic properties (such as those of Salkovitz and Schindler).

The plot of cell volume vs concentration (Fig. 4) shows the discontinuity in the indium-magnesium to best advantage. The plot is linear both above and below the inflection point. Both straight line segments when extrapolated to 0% indium pass through the cell volume of pure magnesium. Thus, indium shows two distinct atomic volumes in magnesium solutions, depending on its concentration. Since the atomic volume of a solute atom should depend primarily on nearest neighbor interactions, the discontinuity in the atomic volume of indium in magnesium suggests a sharp change in nearest neighbor interactions, and consequently a change in short-range order. Such a suggestion would lead to an explanation of the differences in the lattice constant behavior between indium-magnesium and aluminum-magnesium. If one accepts the electronic data as proof that overlap takes place in
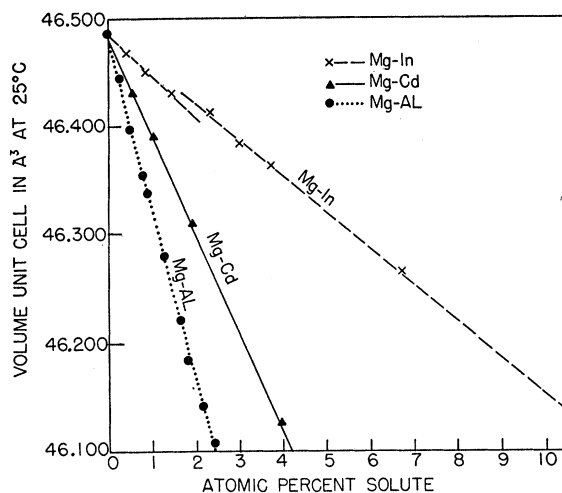
both systems, it would follow that only in indium-magnesium is overlap accompanied by changes in local ordering. That is, overlap may or may not be accompanied by changes in local ordering and it is the latter change which is reflected in the lattice constants. Such a conclusion is highly tentative and must be tested by short-range order measurements on the alloys involved.

IV. SUMMARY

All the experimental evidence for the magnesium-indium alloys shows a sharp change in measured properties between 1.5 atomic percent indium and 2.3 atomic percent indium which can be interpreted in terms of a Brillouin zone model. The magnesium-aluminum alloy curves indicate no significant deviations from linearity in the x-ray data, while measurements of the electronic properties show a break between 1 and 1.3 atomic percent aluminum. The assumption that the break in the axial ratio vs composition curve is a purely electronic effect or more accurately that overlap always gives rise to such a break is not proved by the x-ray data. An alternative explanation based on changes in short-range order of the break in the magnesium-indium lattice constant-concentration curve has been suggested.

V. ACKNOWLEDGMENTS