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Dimensional Analysis of Laves Phases: Observations on the Axial Ratios of Certain Phases with the $MgZn_2$ Structure

BY W. B. PEARSON

Departments of Physics and of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

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Abstract

The a and c cell dimensions of phases with the hexagonal $MgZn_2$ (MN_2) structure vary linearly with D_M and D_N, the diameters of the component atoms for coordination number 12, in series of phases that have the same N or M component respectively. The coefficients of these a and c dependences on D_M and D_N for series of phases formed between the rare earths (M) and Ru, Os, Tc or Re (N) are such as to provide an analytical result, not normally available, that change of axial ratio (c/a) in series of phases with the same N component results from a special adjustment of the c axis of the cell alone. Such behaviour is interpreted in terms of the atomic arrangement in the structure, and this also leads to the prediction that a similar effect should be found in phases with the hexagonal wurtzite structure. This is confirmed insofar as the available data permit. Additional observations are made on the cell dimensions of phases formed by Y, Ca, Sr and Ba (M) with Mg (N), that have the $MgZn_2$ structure.

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1. Introduction

Dimensional analyses have been carried out for phases with both the cubic ($MgCu_2$) and hexagonal ($MgZn_2$) Laves phases, MN_2. The results reported for the cubic phases (Pearson, 1981) are quite complex and the situation is further compounded for phases with the $MgZn_2$ structure because of the variable axial ratio and two variable atomic parameters, x and z, accurate values of which are practically unknown. For this reason the only feature of the analyses to be reported here is some interesting observations concerning the axial ratios of certain of the phases.

2. Analysis

We proceed as discussed in §§1, 2 and 4 of the paper dealing with phases having the $MgCu_2$ structure (Pearson, 1981) and separate phases with the $MgZn_2$ structure into five distinct groups according to their disposition on the near-neighbour diagram (Pearson, 1968) and their a and c dependences on D_M and D_N. One of these groups of phases is that of the rare earths (M) with Ru, Os, Tc, and Re (N). Figs. 1 and 2 show (i) the phases on a near-neighbour-diagram plot, (ii) a, c and c/a as a function of D_M, and (iii) a and c, at a constant D_M value of 3·468 Å, as a function of D_N. From these data the following equations are derived

$$\text{for Ru, Os and Re: } a = 0\cdot65D_M + 1\cdot80D_N - 1\cdot871 \quad (1)$$

$$\text{and for Tc: } a = 0\cdot65D_M + 1\cdot80D_N - 1\cdot839, \quad (2)$$

which reproduce the observed a values with a mean error of $|0\cdot005|$ Å for the 27 phases concerned. If the diameter of Tc is taken as 2·738 Å instead of 2·720 Å as assumed, equation (1) applies also to the Tc alloys. A Tc diameter of 2·738 Å would also improve the plot of a against D_N (Fig. 1).

Fig. 2 shows that the axial ratio, c/a, of these phases varies linearly with D_M and has a dependence thereon that is prescribed by the N component, thus giving the following equations for c in terms of a:

$$\text{Ru: } c = (0\cdot095D_M + 1\cdot347)a \quad (3)$$

$$\text{Os: } c = (0\cdot095D_M + 1\cdot319)a \quad (4)$$

$$\text{Tc: } c = 1\cdot6455a \quad (5)$$

$$\text{Re: } c = (1\cdot738 - 0\cdot03D_M)a. \quad (6)$$

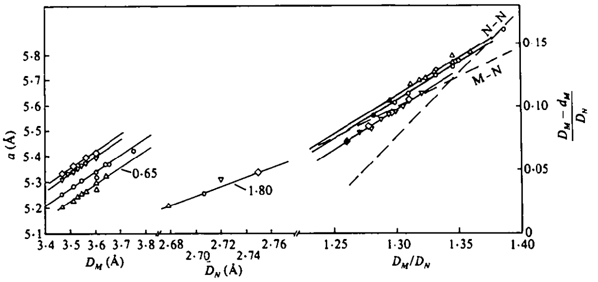

Fig. 1. Rare-earth (M) alloys of Ru, Os, Tc and Re N components. Left: a *versus* D_M. Centre: a for Lu alloys ($D_M = 3\cdot468$ Å) *versus* D_N for N components Ru, Os, Tc and Re. Right: Near-neighbour-diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N for alloys of N components Ru, Os, Tc and Re. The broken lines indicate when the 12–6 M–N distances exactly equal $\frac{1}{2}(D_M + D_N)$ and the 6 N–N distances equal D_N. Alloys of Lu (M) are indicated by filled symbols. N components are indicated by the symbols: △ Ru, ○ Os, ▽ Tc and ◇ Re. Numbers indicate slopes of lines on this and subsequent figures.

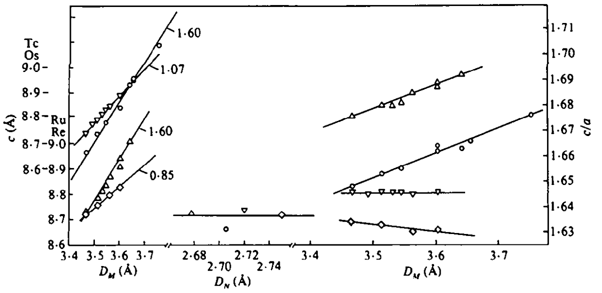

Fig. 2. Rare-earth (M) alloys of Ru, Os, Tc and Re N components. Left: c *versus* D_M. Centre: c for Lu alloys *versus* D_N. Right: axial ratio, c/a *versus* D_M for alloys of N components Ru, Os, Tc and Re. Symbols for the N components are the same as in Fig. 1.

Fig. 2 also indicates that c is essentially independent of D_N for this series of alloys, and from the axial-ratio data the following dependences of c on D_M can be derived which are in agreement with the slopes of c *versus* D_M in Fig. 2:

$$\text{Ru: } c = 1\cdot60D_M + 3\cdot164 \quad (7)$$

$$\text{Os: } c = 1\cdot60D_M + 3\cdot099 \quad (8)$$

$$\text{Tc: } c = 1\cdot07D_M + 5\cdot032 \quad (9)$$

$$\text{Re: } c = 0\cdot85D_M + 5\cdot768. \quad (10)$$

These four equations reproduce the observed c values with a mean error of less than $|0\cdot008|$ Å.

The a cell edge of these phases appears to be controlled by an average of the M–N and N–N contacts weighted according to their multiplicity as indicated by the near-neighbour diagram. The c cell edge on the other hand is controlled mainly by the M–M contacts.

3. Discussion

When for a series of phases with a hexagonal structure, a, c and c/a, say, all increase along the series, there is generally no possible means of determining whether the increase in c/a results from a relative increase in c, a relative decrease in a, or from relative changes in both. Should the change of c/a result from a special adjustment of either a or c alone, it would be necessary to have some way to establish that the variation of one of the cell edges along the series of phases was 'normal'. This is exactly what the analysis of the phases formed between the rare earths and Ru, Os, Tc and Re provides, since the coefficients of the dependence of a on D_M and D_N are the same for all of the phases, regardless of the N component, but the coefficients of the dependence of c/a, or c on D_M are not; they depend on the specific N component. Hence we have a unique analytical solution to the problem which shows that the variation of c/a along the four series of phases results from a special adjustment of c alone. Not only is this adjustment a linear function of D_M (except for Tc alloys where c/a is constant), but it depends also on the specific N component; it is not, however, just a general function of D_M/D_N.

The linear dependence of c/a on D_M in these series of phases with the same N component requires that the contacts in the adamantine arrays of M atoms in the structure must influence the c dimension of the cell. The reason for such behaviour can be seen by comparing projections of the $MgCu_2$ structure on the $(1\bar{1}00)$ plane when it is set in a hexagonal cell, and of the $MgZn_2$ structure on the $(11\bar{2}0)$ plane. Such projections can be found in Fig. 3 of Shoemaker & Shoemaker (1967) or on pages 42 and 43 of Pearson (1972). In each structure, two closely spaced layers of M atoms parallel to the basal planes of the hexagonal cells [(111) plane of cubic $MgCu_2$], are separated from the next double layer by a much greater distance along [0001]. An M atom in the upper of the double layers is bonded to three M atoms in the lower of the double layers, and bonded along [0001] to an M atom of the next double layer above. This of course is the cubic and hexagonal diamond, or sphalerite and wurtzite arrangement of atoms. In the $MgCu_2$ structure all parameters except the four equal M–M distances are fixed by cubic symmetry, but in the hexagonal $MgZn_2$ structure there are two degrees of freedom to be considered – the z parameter of the M atoms allowing their relative movement along [0001] and the axial ratio of the unit cell. Through a combination of these, the M–M distance along [0001] can differ from the three M–M distances between atoms in the double layers. Thus, when the diameter of the M component generally controls the c dimension of the cell, it is expected to do this through the [0001] M–M contacts, with adjustment of z and c/a; hence the observed dependence of c/a on D_M. The effect of these adjustments is expected to be small within the double layers, parallel to the basal plane, that control a; hence they will remain similar to the double layers in the $MgCu_2$ structure.

In these circumstances one could expect (i) that c/a depends on D_M for a series of phases with the same N component, and that the ratio of the coefficients of the dependences of a and c on D_M is not equal to c/a, as is found for the phases formed by the rare earths and Ru, Os and Re, (ii) if in a series of alloys with the same N component, c/a is constant and does not depend on D_M, the ratio of the coefficients of the dependences of a and c on D_M should be equal to the value of c/a, as is observed for phases formed by the rare earths and Tc, and (iii) if indeed the double layers of M atoms in the $MgZn_2$ structure remain essentially unperturbed like those in the $MgCu_2$ structure, the a dependence on D_M and D_N should be the same for all phases, as is observed. Secondly, the ideal relationship $a_{MgCu_2}/a_{MgZn_2} = \sqrt{2}$ might be expected to apply to the ratio of the coefficients of the dependence of a on D_M for phases with two structures that are formed by the same components. There is evidence of such behaviour since a depends on $0{\cdot}923D_M$ for phases with the $MgCu_2$ structure that are formed by the rare earths and Ru or Os (Pearson, 1981), whereas for phases with the $MgZn_2$ structure which are formed by the rare earths and Ru or Os, a depends on $0{\cdot}65D_M$, and $0{\cdot}923/0{\cdot}65 = 1{\cdot}42 \sim \sqrt{2}$.

These expectations are thus reasonably well confirmed, but it must still be noted that the observed dependence of c/a on D_M is particular to the N component. Furthermore, since the adamantine arrays of M atoms in the $MgCu_2$ and $MgZn_2$ structures are the atomic arrangements in the sphalerite and wurtzite structures (neglecting the difference in the component atoms), similar behaviour is predicted for phases with the hexagonal wurtzite structure. Although there are insufficient comparable phases with the wurtzite structure to test the prediction satisfactorily, an indication of its correctness can be gained from the cell dimensions of the GaN and InN (MN) phases. These give $a = 0{\cdot}70D_M + 1{\cdot}212$, $c = 1{\cdot}05D_M + 2{\cdot}215$ and $c/a = 1{\cdot}704 - 0{\cdot}028D_M$. Since a was found to be proportional to $1{\cdot}0D_M$ for the cubic, sphalerite phases (Pearson, 1980a; see Fig. 17), the ideal ratio, $a_{\text{sphalerite}}/a_{\text{wurtzite}} = \sqrt{2} \sim 1{\cdot}0/0{\cdot}70$, is seen to hold for the coefficients of the dependences of a on D_M in the two structures. Hence, the variation of the a cell edge between GaN and InN is seen to be 'normal' and the change of c/a can be attributed to a special adjustment of c, consistent with the apparent dependence of c/a on D_M.

Fig. 3 shows a, c and c/a as a function of D_M, together with a near-neighbour-diagram plot for phases formed by non-rare-earth elements and Mg. An atomic-number rule, previously discovered (Pearson,

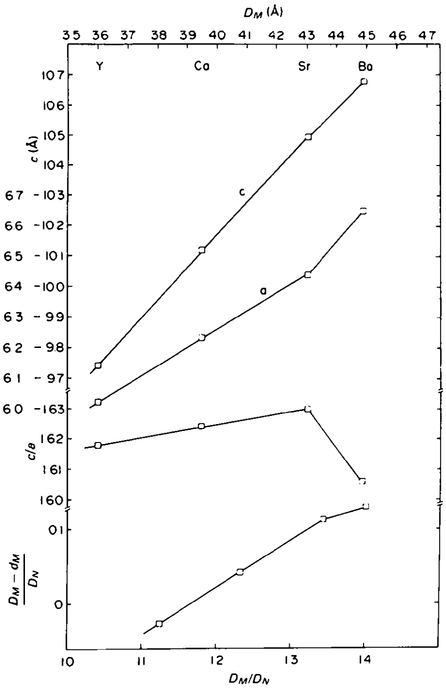

Fig. 3. Alloys of Y, Ca, Sr and Ba (M) with Mg (N) showing a, c and c/a *versus* D_M and a near-neighbour-diagram plot of $(D_M - d_M)/D_N$ *versus* D_M/D_N.

1980*b*), states that for intermetallic phases with a given structure formed by the like elements Ca, Sr and Ba or Sc, Y and La as one component, the cell dimension(s) is a linear function of the atomic numbers of the elements Ca, Sr and Ba or Sc, Y and La. This means that the cell dimension(s) cannot also be a linear function of the CN 12 diameters of these elements; the dimension(s) of the Ba or La phases must be too large to be collinear with those of the Ca and Sr, or Sc and Y phases. The a cell edge of $CaMg_2$, $SrMg_2$ and $BaMg_2$ is a strictly linear function of the atomic numbers of Ca, Sr, and Ba and, accordingly, as seen in Fig. 3, a for $BaMg_2$ is too large for it to be collinear with the (Y), Ca and Sr phases as a function of D_M. On the other hand, c for the four phases of Y, Ca, Sr and Ba is essentially a linear function of D_M, and so the atomic-number rule does not hold for the c dimension of the unit cell of these phases. Therefore, the decreased axial ratio of $BaMg_2$ relative to the other three phases results for the special adjustment of a that is required to satisfy the atomic-number rule. Whether or not the increase of c/a with D_M for the series of phases YMg_2, $CaMg_2$, $SrMg_2$ results from special relative changes in a, c, or both, there is no means of telling.

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The Structure of Triphenylarsine Sulfide

BY S. V. L. NARAYANA AND H. N. SHRIVASTAVA

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Bombay-400 076, *India*

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Abstract

Crystals of $C_{18}H_{15}AsS$ are monoclinic, space group $P2_1/c$, with a = 18·426 (4), b = 9·750 (5), c = 18·582 (4) Å, β = 105·74 (6)°, Z = 8, ρ_c = 1·40, ρ_m = 1·38 Mg m^{-3} and μ(Cu $K\alpha$) = 4·127 mm^{-1}. The two non-equivalent molecules in the asymmetric unit are nearly identical and lack C_{3v} symmetry because of the asymmetric orientation of their phenyl rings around the As—C bonds. The average of six As—C bonds is 1·949 Å, but one, As′—C(13′), is very short [1·854 (6) Å]. The final R factor was 0·086 (R_w = 0·092) for 1675 visually estimated independent reflections. The structure is pseudo $P2_1/a$ type. The geometry at the As atom is approximately tetrahedral with an average As—S distance of 2·090 (6) Å.

Introduction

Krishnan, Datta & Narayana (1977) reported crystal data for compounds formed by the reaction of selenium sulfide, SeS_2, with triphenyl compounds of Group V elements, and started the structure determination of some of them. Meanwhile, Codding & Kerr (1978, 1979) reported the structures of triphenylphosphine sulfide and triphenylphosphine selenide. We now report the structure of triphenylarsine sulfide.

Experimental

A colorless crystal of dimensions 0·30 × 0·25 × 0·32 mm was obtained from benzene solution. Equi-inclination Weissenberg photographs were obtained using Cu $K\alpha$ radiation, λ = 1·5418 Å, covering lattice nets $h0l$ to $h6l$, $0kl$ and $1kl$. 1675 visually estimated intensities were corrected for Lorentz–polarization and spot-extension factors. Systematic absences confirmed the space group $P2_1/c$. Cell dimensions were measured from high-angle spots in Weissenberg photographs taken by the asymmetric mode of film loading (Straumanis & Ievins, 1935). Long exposure to X-rays (*ca* 100 h) turned the crystal light yellow without altering the relative intensities. Absorption corrections have not been applied. The intensities of $h0l$ reflections

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