

weighted according to Rietveld (1966). Observed values can be expressed as $\sum jF_o^2$, where j is the multiplicity factor and the summation extends over the reflexions comprised in one observed peak. These were brought to an absolute scale by comparison with their calculated values.

Five refinement cycles were performed, until the maximum shift of all coordinates was smaller than one-third of their standard deviations. Isotropic temperature coefficients were taken to be:

$$B_{\text{Pb}} = 1.0 \text{ and } B_{\text{F}} = 1.5 \text{ \AA}^2 \text{ for all diagrams.}$$

As the three sets of coordinates were found to be in good agreement, they were averaged according to:

$$\bar{x} = (\sum w_i x_i) / \sum w_i$$

and similarly for z . Here w_i is the reciprocal of the variance of x_i . The standard deviations of the averaged coordinates were computed as $\sigma(\bar{x}) = (\sum w_i)^{-1/2}$. In no case did the difference between the coordinates of the original three sets and the averaged values exceed 1.5σ . The agreement indices computed from the final coordinates and defined by Rietveld (1966), were: 4.4% for pattern *A*, 7.4% for pattern *B* and 5.1% for pattern *C*.

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Some *C11b*-type compounds of Sc, Y and the lanthanides with Cu, Ag and Au. By A. E. DWIGHT, J. W. DOWNEY and R. A. CONNER, JR., *Argonne National Laboratory, Argonne, Illinois, U.S.A.*

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The *C11b* (MoSi_2 type) structure has been studied in twenty compounds of AB_2 stoichiometry. The A elements are Sc, Y and the lanthanide elements Gd through Lu. The B elements are Cu, Ag and Au. Unit-cell constants are given.

Introduction

Several crystal structure types exist in AB_2 compounds in which A is an element from a group to the left of the Mn group in the periodic table and B is an element from either the Mn group or a group lying to the right. Nearly all AB_2 compounds can be classified into three families, as follows: (1) Laves phases, of the MgCu_2 , MgZn_2 , and MgNi_2 types, (2) AlB_2 type and its variant CeCu_2 type, (3) MoSi_2 type and its variant MoPt_2 type. In AB_2 compounds where A is a member of the Sc group (including the lanthanides), and B is a member of the Cu group, there is a competition between the second and third families, *i.e.* CeCu_2 type and MoSi_2 type. The present paper reports crystal structure data for the b.c. tetragonal MoSi_2 -type compounds.

Experimental technique

Alloys were made by arc melting on a water-cooled copper hearth under an argon atmosphere. Sc, Y and lanthanide elements were 99.0% pure, while the copper, silver and gold were 99.9% pure. Weight losses were usually less than 2% of the initial weight for silver alloys and less than 1% for gold and copper alloys. Arc-melted buttons of the alloys were homogenized in evacuated capsules at temperatures from 600 to 900°C. Powder specimens obtained by crushing

Table 4. *Interatomic distances and their standard deviations (in brackets)*

Pb-F(1)	2.64 (1) Å	Pb-F(2)	2.41 (2) Å
	2.53 (2)		2.69 (1)
	2.45 (1)		3.03 (1)

In Table 2 the final coordinates have been listed together with those derived by Byström. It is seen that his structure has been fully confirmed. Table 3 gives the observed and calculated values of jF_o^2 , while in Table 4 Pb-F distances and their standard deviations have been collected. The minimum fluorine-fluorine separation is 2.81 ± 0.02 Å.

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References

- BERG, J. M. VAN DEN (1964). Thesis, Leiden University, p. 24.
 BYSTRÖM, A. (1947). *Ark. Kemi Min. Geol.* **24A**, 1.
 RIETVELD, H. M. (1966). *Acta Cryst.* **20**, 508.
 SAUKA, YA. (1951). *Zh. Fiz. Khim.* **25**, 41.

the homogenized buttons were then heat treated briefly at the same temperature as the homogenization temperature before X-ray diffraction. Some powder specimens were furnace cooled, others were given a water quench. No differences in the resolution of lines, or in the presence of a second phase, could be attributed to the cooling rate.

X-ray powder photographs were taken with Co $K\alpha$ radiation and a Straumanis-type Debye-Scherrer powder camera (114.6 mm diameter). The patterns were identified as tetragonal by use of a Bunn chart, and as body-centered from the observation that $h+k+l=2n$. The stronger lines on the pattern were those for which $l=3n$. The presence of numerous weaker lines, including 002, 101, 004 and 112, for which $l \neq 3n$, required a unit cell containing six atoms, rather than the smaller cell containing two atoms. The observed lattice parameters, extinctions and intensities all indicated that the b.c. tetragonal structure was the *C11b*, of which MoSi_2 is the prototype. Lattice parameters were calculated on the IBM 704 and CDC 3600 computers by the method described by Mueller, Heaton & Miller (1960). The α_1 and α_2 lines of the 226, 323, 109, 400 and 316 reflections were used in the computer solutions.

Results

Table 1 lists unit cell constants and volume ratios for twenty examples of the MoSi_2 -type structures. Eight of these

compounds had been previously reported by Baenziger & Moriarty (1961), and by Moriarty, Gordon & Humphreys (1965) and their data are included in Table 1. Our values for c_0 , a_0 , c/a and volume per formula weight are shown in Fig. 1. The volume per formula weight was obtained by dividing the volume of a unit cell in \AA^3 by 2, since there are two formula weights (six atoms) per unit cell.

As shown in Table 1, the lanthanides from Gd to Lu (except YbAg₂) form the MoSi₂-type structure with Ag or Au. Alloys of La, Ce, Pr, Nd and Sm with Ag or Au in the AB₂ ratio were also investigated, but failed to form the MoSi₂-type structure. The diffraction patterns of these ten alloys were complex and were not identified. We have investigated SmAu₂ in some detail, because, owing to the close resemblance of Sm to Gd, a SmAu₂ compound isostructural to GdAu₂ might be expected. However, we have quenched specimens of SmAu₂ from 600°, 800° and 1000°C, but did not find the MoSi₂-type structure.

ScCu₂ (Table 1) has the MoSi₂-type structure but YCu₂ and 13 of the lanthanide-Cu₂ alloys were shown by Storm & Benson (1963) to have the orthorhombic CeCu₂-type structure, which may be considered to be a variant of the AlB₂-type structure. We have confirmed the CeCu₂-type structure in ErCu₂.

Discussion

It is of interest to inquire whether the stability of the MoSi₂-type structure is dependent on a critical range of relative atomic sizes. In the past the C.N.12 radius of an element in the pure state has been used as an indication of atomic size, but in the present paper we use the atomic volume in place of the radius. The principal reason for avoiding the use of radii as a measure of size is the uncer-

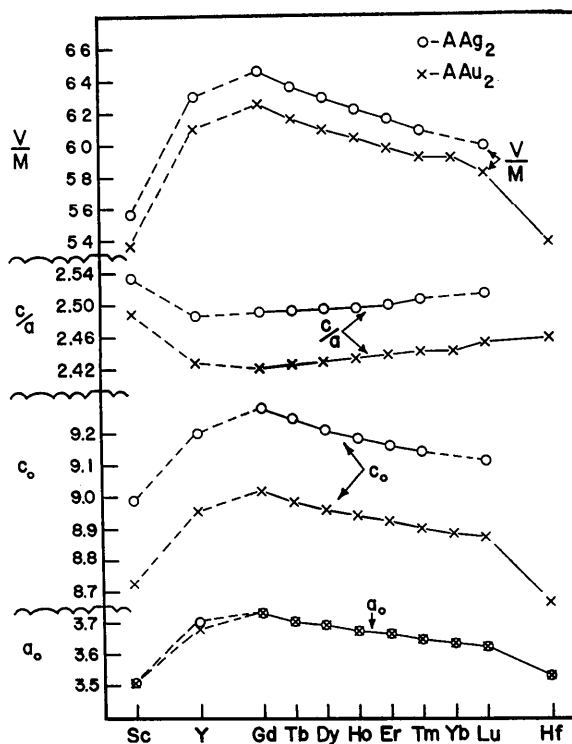


Fig. 1. Unit-cell constants, axial ratios, and volume per formula weight for AAg₂ and AAu₂ compounds which have the MoSi₂-type structure.

Table 1. Lattice parameters of C11b compounds

AB	a_0	c_0	c/a	V_A/V_B
ScCu ₂	3.290 ± 0.001	8.388 ± 0.001	2.550	2.119
ScAg ₂	3.519 ± 0.001	8.922 ± 0.001	2.535	1.462
YAg ₂	3.701 ± 0.001	9.201 ± 0.001	2.486	1.947
GdAg ₂	3.729 ± 0.001	9.287 ± 0.001	2.490	1.930
GdAg ₂ *	3.728 ± 0.001	9.296 ± 0.006	2.494	1.930
TbAg ₂	3.710 ± 0.001	9.247 ± 0.001	2.492	1.871
DyAg ₂	3.695 ± 0.001	9.210 ± 0.001	2.493	1.848
DyAg ₂ *	3.6957 ± 0.0002	9.213 ± 0.001	2.493	1.848
HoAg ₂	3.681 ± 0.001	9.181 ± 0.001	2.494	1.819
HoAg ₂ †	3.682 ± 0.001	9.172 ± 0.004	2.494	1.819
ErAg ₂	3.668 ± 0.001	9.159 ± 0.001	2.497	1.795
ErAg ₂ †	3.668 ± 0.001	9.135 ± 0.002	2.497	1.795
TmAg ₂	3.652 ± 0.001	9.140 ± 0.001	2.503	1.766
LuAg ₂	3.628 ± 0.001	9.113 ± 0.001	2.512	1.725
ScAu ₂	3.508 ± 0.001	8.725 ± 0.001	2.487	1.471
YAu ₂	3.691 ± 0.001	8.959 ± 0.001	2.427	1.959
GdAu ₂	3.728 ± 0.001	9.020 ± 0.001	2.420	1.941
GdAu ₂ *	3.7320 ± 0.0006	9.014 ± 0.003	2.415	1.941
TbAu ₂	3.707 ± 0.001	8.987 ± 0.001	2.424	1.882
DyAu ₂	3.691 ± 0.001	8.961 ± 0.001	2.428	1.859
DyAu ₂ *	3.6940 ± 0.0006	8.956 ± 0.003	2.424	1.859
HoAu ₂	3.677 ± 0.001	8.940 ± 0.001	2.431	1.829
HoAu ₂ †	3.676 ± 0.001	8.934 ± 0.001	2.431	1.829
ErAu ₂	3.662 ± 0.001	8.920 ± 0.001	2.436	1.806
ErAu ₂ †	3.665 ± 0.002	8.932 ± 0.003	2.436	1.806
TmAu ₂	3.648 ± 0.001	8.900 ± 0.001	2.440	1.776
YbAu ₂	3.636 ± 0.001	8.887 ± 0.001	2.444	2.424
LuAu ₂	3.623 ± 0.001	8.875 ± 0.001	2.450	1.735

* Baenziger & Moriarty (1961).

† Moriarty, Gordon & Humphreys (1965).

tainty as to which interatomic distance to use in computing a radius, in the case of complex structures having several different interatomic distances. Values of the atomic volume of pure elements were taken from the paper by Rudman (1965). Table 1 includes a list of relative atomic sizes in terms of the atomic volume of the Sc group element divided by the atomic volume of the Cu group element.

Nevitt (1963) has discussed the MoSi₂-type compounds and has observed that the ideal radius ratio is 1 (hence, the ideal volume ratio is also 1), many compounds having ratios which lie above the ideal value. When MnAu₂ (Hall & Royan, 1959) is also considered, the apparent range in volume ratios is from 0.718 for MnAu₂ to 2.424 for YbAu₂. However, so high a volume ratio for YbAu₂ is of questionable validity, because the atomic volume for pure Yb applies to divalent Yb, but there is reason to believe that Yb in YbAu₂ is nearly trivalent. As shown in Fig. 1, the *c*₀ and *a*₀ values for YbAu₂ lie on a smooth curve between Tm and Lu. The *c/a* and volume per formula weight values show only a small deviation. If Yb were divalent, the unit cell constants would be much larger. This effect was recently discussed by Kripyakevich, Gladyshevskii, Zarechnyuk, Evdokimenko, Zalutskii & Frankevich (1964). Therefore, the volume ratio for YbAu₂ should be computed from a lower unknown volume for trivalent Yb.

A better way to obtain a maximum limiting volume ratio for MoSi₂-type structures is by use of data for Y, Sm, and Gd compounds. The elements Y, Sm and Gd all have nearly the same atomic volume, but when alloyed with Ag and Au, only Y and Gd form the MoSi₂-type structure. Therefore, the maximum limiting volume for the Sc group-Au₂ series must lie close to the value for GdAu₂, *i.e.* 1.941.

A different limiting volume ratio is obtained from the Sc group-Cu₂ series. Only the smallest member of the Sc group, Sc itself, when alloyed with Cu, forms the MoSi₂-type structure (Table 1). The next smallest, Lu, forms the CeCu₂-type (Storm & Benson, 1963). Volume ratios are 2.119 for ScCu₂ and 2.50 for LuCu₂. The limiting volume ratio for the MoSi₂-type structure lies above 2.119 when the B element is Cu, and close to 1.941 when the B element is Au. Therefore, it is concluded that no single value can be assigned as the upper limit, but that the maximum limiting volume ratio is very approximately 2.

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References

- BAENZIGER, N. C. & MORIARTY, J. L., JR. (1961). *Acta Cryst.* **14**, 948.
 HALL, E. O. & ROYAN, J. (1959). *Acta Cryst.* **12**, 607.
 KRIPYAKEVICH, P. I., GLADYSHEVSKII, E. I., ZARECHNYUK, O. S., EVDOKIMENKO, V. I., ZALUTSKII, I. I. & FRANKEVICH, D. P. (1964). *Sov. Physics-Cryst.* **8**, 477.
 MORIARTY, J. L., GORDON, R. O. & HUMPHREYS, J. E. (1965). *Acta Cryst.* **19**, 285.
 MUELLER, M. H., HEATON, L. & MILLER, K. T. (1960). *Acta Cryst.* **13**, 828.
 NEVITT, M. V. (1963). *Electronic Structure and Alloy Chemistry of the Transition Elements*. P. A. Beck, Editor. New York: John Wiley.
 RUDMAN, P. (1965). *Trans. AIME*, **233**, 871.
 STORM, A. R. & BENSON, K. E. (1963). *Acta Cryst.* **16**, 701.

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The space group and lattice constants of the 2-, 3- and 4-iodosalicylideneanilines. By J. L. BERNSTEIN. *Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.*

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The space group and lattice constants of photochromic and thermochromic 2-, 3- and 4-iodo-salicylideneanilines have been determined.

The crystalline *N*-salicylideneanilines exhibit interesting color changes induced by ultraviolet irradiation (photochromic) or by temperature changes (thermochromic). These properties of the salicylideneanilines are a function of the crystal and molecular structure. Thermochromicity requires planar, close packed molecules, whereas photochromicity appears to require nonplanar molecules with a relatively open crystal structure (Cohen, 1964).

An X-ray study of the salicylideneanilines having chlorine or bromine in the 2-, 3- and 4-positions has previously been made (Cohen, Schmidt & Flavin, 1964). The 2-chloro and 2-bromo derivatives are isomorphous and are both photochromic. The 3-chloro- and 3-bromo derivatives are both thermochromic but are not isomorphous.

A recent infrared spectroscopic study (Cohen, 1966) of the phase system of the 4-chloro and 4-bromo derivatives shows that these materials exhibit 'structure mimicry'. (Sacconi, Clampolini & Speroni, 1965). This is the existence of two series of solid solutions in which the guest molecules

(solute) adopt the molecular structures of the host molecules. These systems have been subject to an infrared examination (Dodd & Cohen, 1966) with particular emphasis on the vibrational modes of the halogen atoms. This work was extended to include the 2-, 3- and 4-iodo derivatives. For this purpose it was necessary to obtain structural information on the iodosalicylideneanilines (I). The iodine may be in the 2-, 3- or 4-position as indicated.

In this study, the space groups and lattice constants of the three iodo-substituted compounds have been determined. Precession, Weissenberg and rotation photographs were

