

reported for ribonuclease.<sup>15,20</sup> Two tyrosyl groups are "free" and ionize in a normal way and two are "bound" and ionize much less readily. In view of this fact it is interesting to mention the results of some iodination experiments on horse heart cyt. c, which also contains four tyrosine residues.<sup>21</sup> Thus, Ishikura *et al.*<sup>22</sup> found that 4 iodine atoms were readily (within 1 min) incorporated into the hemoprotein at pH 7.0, corresponding to the iodination of two tyrosine residues, which resulted in a complete loss of its electron transferring activity. The iodination of the other residues was found to proceed at a much slower rate.

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## On the Crystal Structure of MoAs<sub>2</sub>

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In a recent study of molybdenum arsenides, the existence of a previously unknown phase with composition MoAs<sub>2</sub> has been established.

Samples were prepared from 99.9% pure molybdenum (L. Light & Co., Ltd.) and 99.999% pure metallic arsenic (Johnson, Matthey & Co., Ltd.). Samples with composition 60.00, 65.52, 66.67, 67.74, and 75.00 atomic % As were made by heating accurately weighed quantities of molybdenum and arsenic in evacuated and sealed silica tubes. The samples were heated at 600°C for 5 days, and quenching in ice water as well as slow-cooling was used.

All samples were crushed and X-ray photographs taken in a Guinier focusing camera of 80 mm diameter with strictly monochromatized CuK $\alpha_1$ -radiation. For the calculation of lattice constants potassium chloride (Analar, The British Drug Houses, Ltd.,  $a = 6.2919 \text{ \AA}^3$ ) was added as an internal standard. Lattice constants are expressed in Ångström units on the basis of  $\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$ . Densities were determined by the pycnometric method at 25°C with kerosene as displacement liquid.

In the molybdenum-arsenic system three intermediate phases have been identified. Two of the phases with approximate compositions MoAs<sub>0.8</sub> and MoAs<sub>1.4</sub> will be the subject of a forthcoming paper;<sup>2</sup> and only the structural properties of the third phase, MoAs<sub>2</sub>, will be discussed here. Guinier photographs of this phase, cf. Table I, could be indexed on the basis of a monoclinic unit cell with dimensions:

Table 1. Guinier photograph data of MoAs<sub>2</sub> taken with strictly monochromatized CuKα<sub>1</sub>-radiation.

<i>I</i> <sub>obs</sub>	sin <sup>2</sup> θ × 10 <sup>5</sup>		<i>hkl</i>	<i>I</i> <sub>obs</sub>	sin <sup>2</sup> θ × 10 <sup>5</sup>		<i>hkl</i>
	obs	calc			obs	calc	
w	1312	1312	001	w	24578	24577	51 $\bar{3}$
m	2929	2921	20 $\bar{1}$	w	24717	24717	22 $\bar{1}$
w	3804	3798	200	w	25634	25634	220
w	4666	4667	20 $\bar{2}$	w	25634	25645	20 $\bar{5}$
vw	5217	5246	002	w	25805	25808	312
w	6405	6399	110	vw	26085	26096	40 $\bar{5}$
vw	6618	6616	11 $\bar{1}$	vw	26292	26291	60 $\bar{3}$
vst	8801	8805	111	vw	26292	26299	60 $\bar{2}$
st	9027	9037	20 $\bar{3}$	w	28924	28906	604
st	9444	9456	11 $\bar{2}$	w	28924	28930	60 $\bar{1}$
m	11656	11685	40 $\bar{2}$	w	29214	29189	510
st	11774	11805	003	w	29214	29195	402
m	12079	12127	40 $\bar{1}$	w	30375	30370	31 $\bar{5}$
st	12651	12675	31 $\bar{2}$	w	30850	30833	22 $\bar{3}$
st	13837	13834	112	w	31781	31763	114
st	13988	13995	310	w	33487	33481	42 $\bar{2}$
m	14911	14920	11 $\bar{3}$	m	33907	33924	42 $\bar{1}$
st	15201	15193	400	w	34151	34144	60 $\bar{5}$
st	15948	15950	31 $\bar{3}$	w	35645	35650	313
w	16025	16029	204	w	35645	35661	42 $\bar{3}$
w	20876	20883	401	m	35979	35973	511
st	21802	21796	020	m	36983	36989	420
m	22182	22170	203	w	37840	37826	224
w	23006	23007	114	w	40121	40131	403
w	23497	23491	51 $\bar{2}$	st	40802	40799	71 $\bar{3}$

$$a = 9.069 \text{ \AA}, b = 3.2996 \text{ \AA}, c = 7.717 \text{ \AA}, \\ \beta = 119.36^\circ.$$

The approximately constant lattice dimensions for samples of different composition indicate that the homogeneity range must be rather narrow.

The composition was estimated to be MoAs<sub>2</sub> using the disappearing phase method on the Guinier photographs and was ascertained by density measurements.

The observed density of MoAs<sub>2</sub>, 8.07 g cm<sup>-3</sup>, indicates that the unit cell contains 4 (*Z*<sub>c</sub> = 3.98) MoAs<sub>2</sub>-groups. The calculated density of MoAs<sub>2</sub> from the X-ray measurements is 8.11 g cm<sup>-3</sup>.

The *hkl* reflections are absent when  $h + k = 2n + 1$  and the characteristic space groups are accordingly *C2*, *Cm*, and *C2/m*.

A monoclinic structure with this composition and similar unit cell dimensions has recently been observed for NbAs<sub>2</sub>,<sup>3-6</sup>

NbSb<sub>2</sub>,<sup>4-6</sup> TaAs<sub>2</sub>,<sup>3,7</sup> and TaSb<sub>2</sub>.<sup>7</sup> As there were obvious relationships between the intensities of the reflections from MoAs<sub>2</sub> and NbAs<sub>2</sub>, the possibility of the compounds being isostructural was investigated. According to Furuseth and Kjekshus<sup>8</sup> the atomic arrangement in the NbAs<sub>2</sub> structure in terms of the space group *C2* is as follows:

$$(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0) + \\ 4 \text{ Nb in } (c) \quad x, y, z \quad \bar{x}, y, \bar{z} \\ \text{with } x_1 = 0.34, y_1 = \frac{1}{2}, \\ z_1 = 0.30 \\ 4 \text{ As}_I \text{ in } (c) \text{ with } x_2 = 0.09, y_2 = 0.49, \\ z_2 = 0.39 \\ 4 \text{ As}_{II} \text{ in } (c) \text{ with } x_3 = 0.14, y_3 = 0.07, \\ z_3 = 0.03$$

(The values of the variable parameters have been rounded off.) These parameters were used in the calculation of intensities on the Guinier photographs. A reasonable agreement between observed and cal-

culated intensities was obtained indicating that the proposed structure is correct. Further refinement of the parameters was not attempted.

A discussion of the chemical bonding in  $\text{MoAs}_2$  must await further data. It should nevertheless at this stage be mentioned that the existence of a molybdenum arsenide with the  $\text{NbAs}_2$  type structure was somewhat unexpected on the basis of our predictions from the general (8-N) rule. (For details reference is made to Furuseth and Kjekshus.<sup>6</sup>) The existence of  $\text{MoAs}_2$  would for example have been satisfactorily accounted for by the general (8-N) rule assuming one unpaired  $d$ -electron on each Mo atom. Localized, unpaired  $d$ -electrons are inconsistent with  $\text{MoAs}_2$  being diamagnetic.<sup>2</sup>

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## A Note on the Synthesis of Selenourea

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The synthesis of selenourea from hydrogen selenide and cyanamide was first reported by Verneuil.<sup>1</sup> Later several

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modified procedures have been described (*cf.*, e.g. Houben-Weyl).<sup>2</sup>

With concentrated solutions of cyanamide being commercially available at low cost, the synthesis can now be performed quite simply. A preparation was carried out the following way.

Aluminum selenide from 140 g Se was coarsely ground and transferred to a 500 ml flask equipped with an inlet for nitrogen carrier gas, a separating funnel with pressure equalizer, and a gas outlet. Water was added through the funnel, quite slowly in the beginning in order to avoid overheating. The hydrogen selenide that formed was led (through Tygon tubing) into a wash bottle containing 125 ml of a 50 % cyanamide solution (supplied by American Cyanamid Company). The bottle with the reaction mixture was kept in a bath at about 40°C throughout the run. After about 2 h crystals started to separate. On completion of the run, which took a day, the mixture was cooled in ice and filtered under a nitrogen atmosphere. The product was washed with a little ice water and dried over  $\text{P}_2\text{O}_5$ . Yield 90 g. Due to decomposition the melting point is difficult to establish. However, on the Kofler bench it appears to be around 235°C, somewhat higher than has been reported earlier.<sup>3</sup> The dried product was analyzed for C, H, N. (Found: C 9.9; H 3.5; N 23.5. Calc. for  $\text{SeCN}_2\text{H}_2$ : C 9.8; H 3.25; N 22.8). The substance has been kept in a refrigerator for an extended period of time with no apparent change other than a moderate darkening.

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