



## HIGH-PRESSURE HIGH-TEMPERATURE EXPERIMENTS ON $\delta$ -MoN

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High-pressure (6 GPa) high-temperature (1800 K) experiments on hexagonal  $\delta$ -MoN were performed in an attempt to transform this phase to the cubic B1-MoN phase. No transformation was observed. The structure of  $\delta$ -MoN after the high-pressure treatment was refined from X-ray powder diffraction data and found to consist of a NiAs-type related arrangement of Mo atoms which form triangular clusters and N atoms which are situated in trigonal prismatic holes. The superconducting critical temperature reached  $T_c = 15.1$  K. These are the first measurements on well characterized  $\delta$ -MoN samples.

### Introduction

Theoretical [1] as well as empirical [2] considerations suggested that cubic MoN with stoichiometric NaCl-type structure, also called B1-MoN, might be a high-temperature superconductor. An equilibrium phase,  $\gamma$ -MoN<sub>x</sub>, with NaCl structure, occurs only for nitrogen deficient concentrations,  $0.39 < x < 0.54$  [3], while the phase at stoichiometric composition,  $\delta$ -MoN, has a primitive hexagonal metal atom arrangement with doubled sublattice parameters due to clustering [4]. The N atom arrangement is unknown, but the space-group symmetry proposed (P6<sub>3</sub>/mmc [4]) implies a disordered distribution in the trigonal prismatic holes. Both phases are superconducting with transition temperatures of  $T_c = 5.0$  K and  $T_c = 12.0$  K, respectively [5]. As the structure of  $\delta$ -MoN might have a lower degree

of compactness than stoichiometric B1-MoN [1,2], we were led to attempt high-pressure high-temperature experiments which could possibly stabilize B1-MoN, by using an anvil equipment. While this work was in progress, reports on isostatic pressure [6] and belt-type pressure experiments [7] have appeared in the literature.

### Experimental

MoCl<sub>5</sub> was used as starting material and was reacted in a NH<sub>3</sub> gas flow at 920 K to form powdered  $\delta$ -MoN [8]. The powder was then pressed into pellets of 2.8 mm diameter and 3 mm length. The samples were placed into boron nitride crucibles surrounded by graphite heaters in pyrophyllite cubes 10x10x10 mm<sup>3</sup>. The high-pressure heat treatments were performed

with a multianvil cubic device [9] up to 6 GPa and 1800 K. They were then systematically investigated by A.C. susceptibility measurements, X-ray Guinier-Nonius or Guinier-Hägg diffraction photographs (Co and Cu  $K_\alpha$  radiation), and metallographic analysis. Structure refinements were performed on integrated intensities obtained from microdensitometer data [10] by using the X-ray 76 program system [11].

### Results

The experimental conditions of the various high-pressure high-temperature experiments, the resulting superconducting critical temperatures,  $T_c$ , the transition widths,  $\Delta T_c$ , and the hexagonal lattice constants of  $\delta$ -MoN, including those of the starting material, are summarized in Table 1. The most striking result is the increase of  $T_c$  as a function of annealing temperature, from 3.2 K for the starting material up to 15.1 K after 15 minutes at 1800 K under 6 GPa pressure. The values of  $T_c$  increase also with annealing time, whereas  $\Delta T_c$  decrease

(see e.g. run nr 3 and 4, 6 and 7). No trace of the cubic B1-MoN phase is observed in any of the X-ray powder diffraction patterns. Those of the samples annealed below 1300 K are relatively diffuse, which correlates with low values of  $T_c$ . For samples annealed above that temperature, recrystallization is observed both from a sharpening of the diffraction lines (Fig.1) and from metallography (Fig.2). For these samples  $T_c$  rises above 11 K. Addition of small amounts of Nb or Zr as suggested from theoretical considerations [12] do not affect  $T_c$ .

In the X-ray patterns containing sharp diffraction lines, new superstructure reflections appeared which required a doubling of the unit cell along a and c with respect to that of the starting material, as found previously [4]. The systematically absent reflections (hhl and 00l with  $l = 2n+1$ ) indicated five possible space groups. Intensity simulations and structure refinements based on the metal substructure model reported [4] for centrosymmetric space-group  $P6_3/mmc$  and assuming a disordered N atom distribution gave unsatisfactory results ( $R = \Sigma(F_{obs} - F_{calc}) / \Sigma F_{obs}$

Table 1

run nr <sup>a)</sup>	reacting temp./time (K/hrs)	$\Delta T_c$ <sup>b)</sup>		a (Å)	c (Å)	V (Å <sup>3</sup> )
		$T_c$ <sup>c)</sup> (K)	$T_c$ <sup>c)</sup> (K)			
starting material		1.9	3.2	2.850(1)	2.784(2)	19.58(2) <sup>d)</sup>
1	770 / 9	2.1	3.7			
2	1020 / 6	3.8	6.4			
3	1270 / 3	2.8	13.2	5.737(2)	5.613(5)	160.0(2)
4	1270 / 1	6.1	11.7			
5 +25%Nb	1270 / 2	3.0	13.1			
6	1520 / 2	1.9	14.5	5.745(2)	5.619(2)	160.7(1)
7	1520 / 0.16	2.9	11.0	5.741(1)	5.617(1)	160.3(1)
8 +5%Zr	1520 / 0.5	5.9	12.7			
9 +5%Nb	1520 / 0.16					
	1270 / 4	1.2	12.9			
10	1770 / 0.25	1.9	15.1	5.745(1)	5.622(1)	160.7(1)

a) All experiments were performed under a pressure of 6 GPa, except run nr 4 (8 GPa). b)  $\Delta T_c$  between 10% and 90% of the inductive transition (73 Hz). c) At 10% of the transition. d) corresponding to the primitive hexagonal metal atom arrangement.

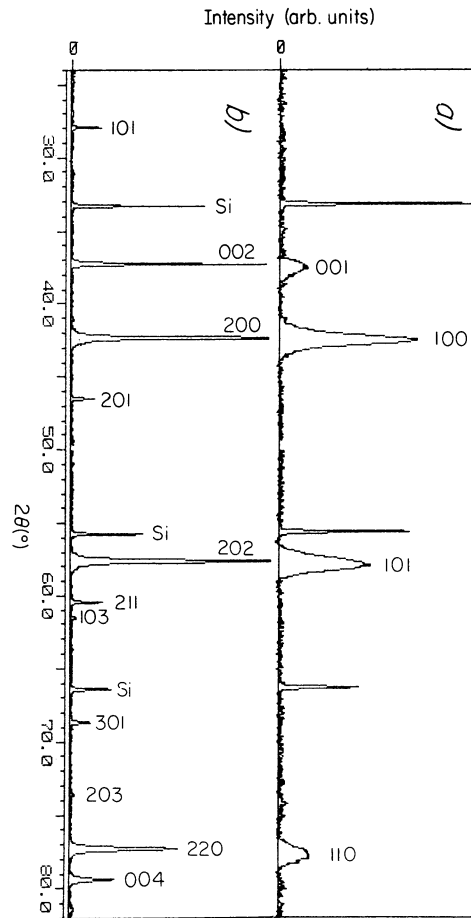


Figure 1

X-ray diffraction patterns of  $\delta$ -MoN with  $\text{Co } K_{\alpha}$  radiation. a) Starting material. Simple hexagonal lattice. b) Annealed sample (nr 10). Unit cell has been doubled. Note the presence of reflections 201 and 203.

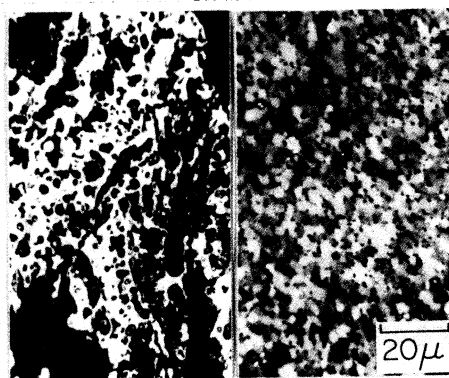


Figure 2

Metallography of (left) starting material and (right) annealed  $\delta$ -MoN (nr 10, magn. 600x). High  $T_c$  are observed only in case of recrystallisation, as shown here and correspondingly in Fig.1b).

= 0.08 for 20 reflections, including those with null intensity). In particular that model could not reproduce some weak reflections such as hkl = 201 and 203. Among the models based on the four space groups left, that in the non-centrosymmetric space-group  $P6_3mc$  allowed an ordered N atom distribution and refined satisfactorily ( $R = 0.06$  for 20 reflections, 5 variables: scale factor, overall temperature factor and 3 positional parameters). The N atoms were fixed in every second trigonal prismatic hole, and allowed to simulate all weak reflections. Results are summarized in Table 2.

The absence of a N-deficient  $\gamma$ -MoN<sub>x</sub> phase in our annealed samples suggests that the N losses during annealing are negligible. The unexpected increase of the unit cell volume for the annealed samples (3% or 4 Å<sup>3</sup> with respect to the superstructure cell) led us to perform both carbon analysis (0.08(1) mole-% before experiment, 0.5(2) mole-% after) and density measurements ( $\rho_{27^\circ C} = 8.10(3)$  g/cm<sup>3</sup> for sample nr 7,  $\rho_{calc} = 9.11$  g/cm<sup>3</sup>). Thus the structure contains only very little carbon, and the difference between the measured and the calculated density is presumably due to residual porosity.

### Discussion

In view of the absence of any trace of the cubic B1-MoN phase after high-pressure high-temperature annealing of our  $\delta$ -MoN samples, a pressure-driven transition from  $\delta$ -MoN to B1-MoN does not seem to exist under the experimental conditions used in our experiments.

Consequently, either the pressure-temperature range actually achievable in our laboratory is not sufficient for such a conversion, as suggested also from a theoretical study [13], or the relative stability of the  $\delta$ -phase is higher than that of B1-MoN throughout the pressure-temperature phase diagram. No other hydrostatic pressure experiments on bulk  $\delta$ -MoN have been reported in the literature as yet. Isostatic high-pressure (1.6 GPa N<sub>2</sub> gas) experiments yielded a mixture of  $\gamma$ -Mo<sub>2</sub>N and  $\delta$ -MoN [6]. Interestingly, a conversion from B1 to  $\delta$ -MoN under 6 GPa pressure has been observed [7] by authors who prepared B1-MoN films [14-16].

The superconducting critical temperature  $T_c = 15.1$  K of our sample which was annealed at 1770 K under 6 GPa (run nr 10) is the highest value observed so far for single phase  $\delta$ -MoN. Somewhat lower values were reported for a mixture of MoS and BN annealed at 1270 K under 4 GPa ( $T_c = 14.8$  K [17]), and for thin films annealed at 1270 K under 6 GPa ( $T_c = 14.9$  K [14]). The only higher value reported so far is that for Mo foils which were annealed at 1720 K under a N<sub>2</sub>-gas pressure of 1.6 GPa ( $T_c = 15.9$  K, table 1 of [6]). However this treatment resulted in a mixture of  $\delta$  and  $\gamma$ -phase, and only a lower value ( $T_c = 13.3$  K) was discussed by these authors in the rest of their paper.

The increase of  $T_c$  in our  $\delta$ -MoN samples is presumably due to small structural changes which are induced by the heat treatment. In fact, the structure model proposed in this work is the first which introduces both a clustering of the

Table 2 : Structural data

Space group $P6_3mc$ (nr 186) :	a = 5.745(1) Å		
	c = 5.622(1) Å		
	x	y	z
Mo(1) 2a :	.0	.0	.250(2)
Mo(2) 6c :	.490(1)	-x	.250(2)
N(1) 2b :	1/3	2/3	.50(-)*
N(2) 6c :	.1667(-)*	-x	.00(-)*

Estimated standard deviations are given in parentheses. \* fixed.

Mo atoms and an ordered arrangement of N atoms. As shown in Fig.3, the atomic arrangement corresponds to that of a deformed NiAs-type structure. Interatomic distances are [Mo-Mo] =

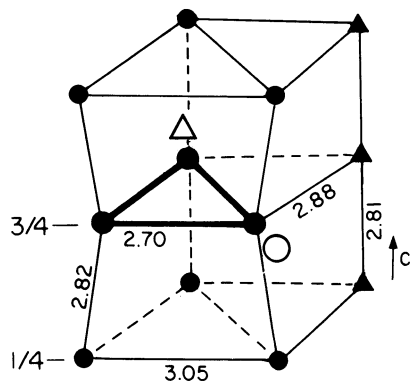


Figure 3

Partial structure of  $\delta$ -MoN (one fourth of the unit cell). Filled symbols, Mo atoms at  $z = 1/4$  and  $3/4$ . Empty symbols, N atoms at  $z = 1/2$  and  $1/1$ . Triangles, Mo(1), N(1). Circles, Mo(2), N(2). Thick line, Mo<sub>3</sub> cluster.

2.70(1) Å within, and 3.04(1) Å between the triangular Mo<sub>3</sub> clusters in a plane perpendicular to the  $c$  axis, as compared to 2.87 Å in a regular NiAs-type structure. The Mo-N distances within the deformed trigonal Mo prisms range between 2.1-2.3 Å, and the shortest N-N distances are 2.9 Å. The role of the clustering of the Mo atoms for the increase of  $T_c$  has been discussed previously [17]. However, in view of our structural results, the ordering of the N atoms could also play a role. It is known that the ordering of both Mo and N sites, but also the N content may affect  $T_c$  [18,19].

In conclusion, it does not seem to be possible to stabilize stoichiometric B1-MoN under the experimental conditions actually available in laboratories. However, annealing of  $\delta$ -MoN under pressure above 1200K promotes the formation of a phase with an ordered structure and improves significantly its superconducting transition temperature.

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#### References

- 1 W.E.Pickett, B.M.Klein and D.A.Papaconstantopoulos, *Physica* **170B**, 667 (1981).
- 2 Y.Zhao and S.He, *Solid State Commun.* **45**, 281 (1983).
- 3 H.Jehn and P.Ettmayer, *J.Less-Common Metals* **58**, 85 (1978).
- 4 N.Schönberg, *Acta Chem.Scand.* **8**, 204 (1954).
- 5 B.W.Roberts, *J.Phys.Chem.Ref.Data*, **5**, 581 (1976).
- 6 A.Morawski, B.Cendlewska and B.Gren, *Physica* **139,140B**, 645 (1986).
- 7 H.Ihara, M.Hirabayashi, K.Senzaki, Y.Kimura and H.Kezuka, *Phys.Rev.* **B32**, 1816 (1985).
- 8 W.Lengauer and P.Ettmayer, to be published.
- 9 F.Haenssler, J.L.Jorda and J.Muller, *Proc. VII Intern. AIRAPT Conf., Le Creusot, France* (1979).
- 10 K.E.Johansson, T.Palm and P.E.Werner, *J.Phys.* **E13**, 1289 (1980).
- 11 J.M.Stewart, P.A.Machin, C.W.Dickinson, H.L.Ammon, H.Heck and H.Flack, *The X-ray 76 System, Tech.Rep.TR-446, Computer Science Center, Univ.of Maryland, College Park* (1976).
- 12 K.Schwarz, D.S.Yee, J.J.Cuomo and J.M.E.Harper, *Phys.Rev.* **B32**, 5489 (1985).
- 13 L.L.Boyer, B.M.Klein and W.E.Pickett, *Physica* **135B**, 252 (1985).
- 14 H.Ihara, Y.Kimura, K.Senzaki, H.Kezuka and M.Hirabayashi, *Phys.Rev.* **B31**, 3177 (1985).
- 15 G.Linker, R.Smithey and O.Meyer, *J.Phys.F* **14**, L115 (1984).
- 16 G.Linker, H.Schmidt, C.Politis, R.Smithey and P.Ziemann, *J.Phys.F* **16**, 2167 (1986).
- 17 J.M.Vandenberg and B.T.Matthias, *Mat.Res.Bull.* **9**, 1085 (1974).
- 18 L.E.Toth, *Transition Metal Carbides and Nitrides* (Academic press, New York, 1971).
- 19 D.A.Papaconstantopoulos and W.E.Pickett, *Phys.Rev.* **B31**, 7093 (1985).