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Determination of the crystal structure of δ-MoN by neutron diffraction

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Abstract

We have determined the crystal structure of ordered hexagonal δ-MoN by use of powder X-ray diffraction and time-of-flight neutron diffraction. A disordered variety of the compound was first prepared by high-temperature ammonolysis of $MoCl_5$. This material has hexagonal symmetry with the space group $P6_3mc$ with $a = 2.87(2)$ and $c = 2.81(1)$ Å. Upon high pressure annealing, the N-atoms become ordered and the unit cell doubles in size: $a = 5.73659(10)$ and $c = 5.61884(17)$ Å. The superconducting transition temperature increases from 4 K in the disordered compound to 12.1 K in the ordered phase.

Keywords: Hardness; MoN; Neutron diffraction; High pressure; Structure determination

1. Introduction

Various physical properties, including high hardness, high melting points, and high T_c superconductivity, make the transition metal nitrides of industrial importance as well as of academic interest. The stoichiometric hexagonal phase of molybdenum nitride (δ-MoN) is a high-hardness material with a low compressibility (bulk modulus $K_0 = 345$ GPa) [1], and it is found to be superconducting. Transition temperatures ranging from 4 to 12 K have been recorded, depending upon the preparation and annealing conditions [2]. It has been determined that the superconducting T_c depends upon the ordering of N-atoms within the hexagonal metal sublattice. However, the crystal structure of this material has not been determined reliably to date, and in particular, the nitrogen positions have not been located with certainty. Here we have used a combination of powder X-ray diffraction methods and time-of-flight (TOF) neutron diffraction studies to determine the crystal structure and to locate the N-atom positions.

Various methods have been used to synthesize molybdenum nitride materials, including direct nitridation of molybdenum powder in an ammonia atmosphere at 1000 K [3], high pressure N_2 nitridation of Mo wire [4], and reaction between MoO_2 and NH_4Cl at 20 kbar and 1800 K [5]. Often, a mixture of MoN_x phases are obtained, primarily cubic Mo_2N and hexagonal δ-MoN. The Mo–N phase diagram was determined by Hagg [3]. In the present work, we used the method of Lengauer [6] to first prepare a N-atom disordered sample of δ-MoN by ammonolysis of $MoCl_5$ at 943 K. The chloride is liquid at this temperature, and the nitride product forms as a fine grained powder. The synthesis conditions were optimized to yield nearly pure stoichiometric δ-MoN. This material was then treated at high pressure and high temperature in a multi-anvil apparatus to yield fully ordered δ-MoN, as described by Bezinge [2]. The products were examined using powder X-ray diffraction and TOF neutron diffraction. The superconducting T_c's were determined by SQUID magnetometry.

Previous structural studies of δ-MoN materials have been carried out using X-ray diffraction. Troitskaya [7] originally proposed the hexagonal space group $P\bar{3}m1$, while Schönberg [8] suggested the hexagonal space

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group $P6_3/mmc$ (194). Following their high-pressure synthesis and structural characterization of the material, Zhao and Range appeared to confirm the $P6_3/mmc$ structure for MoN [5], containing Mo atoms on $2b$ (0,0,1/4) and $6h$ $(x, 2x, 1/4)$ $x = 0.48(9)$ positions, and the N-atoms located on $2a$ (0,0,0) and $6g$ (1/2,0,0) sites. However, recent theoretical calculations indicated that this structure is not stable [9]. Bezinge et al. noted that the space group for the high pressure phase is $P6_3/mc$ and upon high pressure annealing the unit cell axes doubled in size from $a = 2.850$ and $c = 2.784$ Å to 5.737 and 5.613 Å, respectively, and that superstructure reflections appeared in the X-ray diffraction pattern, although the space group remained the same [2]. Here, we used a combination of X-ray and neutron diffraction techniques to determine the crystal structure and N-atom ordering pattern of the ordered δ-MoN compound, prepared by solid-state synthesis followed by annealing at high pressure and high temperature.

Light atoms such as nitrogen scatter X-rays weakly, and so their positions can not be determined accurately using X-ray diffraction, especially with powder methods, in the presence of heavy metals such as molybdenum. It is then best to use neutron diffraction to determine the structures of materials such as MoN. The bound coherent scattering lengths of Mo and N are 5.7 and 11.01 barns, respectively [10], so that it is a simple matter to differentiate between scattering from the metal and N-atoms, and thus model the total structure. Sample amounts obtained from high pressure synthesis runs, such as those carried out in the multi-anvil press, are generally very small (often on the order of only a few mg). This usually prohibits neutron diffraction experiments, that generally require much larger amounts of sample. However, the very high flux of the ISIS spallation source, combined with the very high sensitivity of the newly developed GEM diffractometer, makes it possible to obtain high-quality diffraction patterns from very small samples within a reasonable counting time [11]. In the present case, we have obtained high-quality refineable TOF neutron diffraction patterns from a 6 mg sample of δ-MoN within one hour—a record for the instrument—at both ambient and low temperatures, throughout the superconducting transition temperature range.

2. Experimental

The ammonolysis of $MoCl_5$ was carried out inside a sealed stainless-steel tube with high temperature and pressure valves at either end mounted inside a tube furnace. All connections were made using stainless-steel tubing and fittings. An NH_3 cylinder was attached to the inlet, and two water traps to absorb excess ammonia as well as HCl gas produced during the reaction were placed at the outlet end. $MoCl_5$ (Aldrich 99.999%) powder was spread as a thin layer on Mo foil (Goodfellow 99.9%) in an alumina boat in the center of the furnace. NH_3 (microfine grade) was then passed over the sample and heated at 933 K for three hours. The tube was then sealed and cooled to room temperature. The presence of nearly phase-pure MoN was confirmed by powder X-ray diffraction using a Siemens D500 diffractometer with Cu$K\alpha$ radiation (Fig. 1). The sample consisted of an N-disordered δ-MoN material, as described by Bezinge et al. [2]. Approximately 50 mg of the disordered sample was then subjected to 6 GPa and heated to 1800 K for 60 min using a Walker-type multi-anvil press, using BN capsules contained within Mino Yogio Cr:MgO octahedra and using a graphite furnace.

TOF neutron diffraction experiments were collected on beam line S7 using the GEM station at the ISIS, Neutron Spallation Source, Rutherford Appleton Laboratory, Chilton Didcot, UK. 6 mg of the ordered δ-MoN was loaded into a 3 mm diameter vanadium canister mounted in the sample chamber that was then evacuated to 10^{-4} mbar. The pattern was collected using the 90° detector with a TOF range of 2–16 ms. Data were collected for 4 h at room temperature for the ordered phase. Data were also collected for the ordered phase at low temperature both above and below the superconducting transition temperature determined by our SQUID measurements. The sample was loaded into a closed cycle helium refrigerator and diffraction patterns obtained at 7, 11, 13 and 15 K. The raw data were summed and the sample chamber contribution to the background removed using in-house RAL software. Rietveld profile analysis was then carried using the GSAS suite of programs [12]. The profile coefficients were obtained from the instrument parameter file

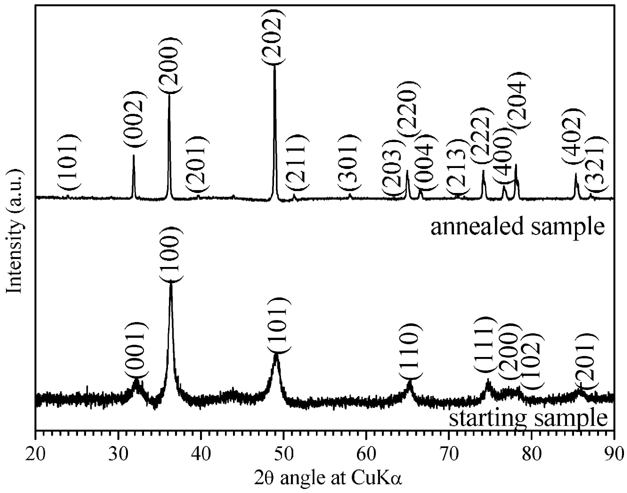

Fig. 1. X-ray diffraction pattern of δ-MoN before (bottom) and after high pressure annealing (top) at 290 K.

produced in house at RAL and consisted of a convolution of the Ikeda-Carpenter (to allow for the moderator pulse shape) and pseudo-Voight functions [13]. No refinement of profile parameters was found necessary to complete the analysis; the background consisted of a power series function with four parameters [12]. For Rietveld analysis of the X-ray data a pseudo-Voight function was used to describe the peak shape and a shifted Chebyshev polynomial background with four co-efficients was used.

The magnetic susceptibility of the samples was measured using a Quantum Design SQUID magnetometer. Each sample was first cooled to 2 K in the absence of a magnetic field (i.e., zero field cooled: ZFC), and then with 1 kG field applied the DC susceptibility was measured as a function of increasing temperature. The sample was then cooled again in the presence of the magnetic field (field cooled—FC) and the measurement repeated. The experiment was performed using both ordered and disordered δ-MoN phases.

3. Results and discussion

Single phase δ-MoN was synthesized by high-temperature ammonolysis treatment of $MoCl_5$. The resulting X-ray diffraction pattern could be indexed to a material with space group $P6_3/mc$, with lattice parameters $a = 2.87(2)$ Å and $c = 2.81(1)$ Å. However, as suggested by Bezinge [2] the N-atoms are disordered in this phase, and the X-ray diffraction pattern of the material exhibits broadened lines (Fig. 1). Upon high pressure annealing the sample shows dramatic decrease in line width and also a change in diffraction pattern, this results in a doubling of the unit cell (Fig. 1) and ordering molybdenum atoms and nitrogen atoms as previously noted by Bezinge et al. [2].

Rietveld refinement was carried out on the X-ray diffraction pattern of the ordered MoN and the results are shown in Fig. 2. Detailed in Table 1 are structural parameters obtained from the Rietveld profile analysis. We note that the atom sites do not show full occupancy from the analysis of the X-ray data. This is a result of the inherent problems of determining crystal structure using X-rays when there are both light and heavy atoms preset in the material. It is necessary to use neutron diffraction to obtain these structural details, and the correct site occupancies.

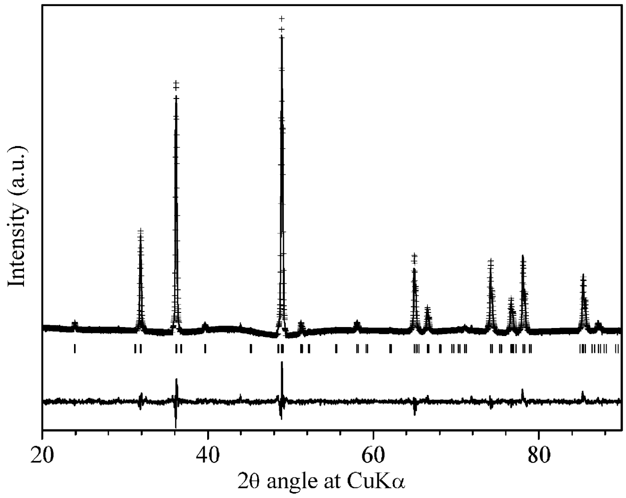

Fig. 2. The X-ray observed (+) and calculated (−) profile and difference profiles (bottom trace) for δ-MoN at 290 K.

Table 1
Results of Rietveld refinement of neutron and X-ray diffraction data for δ-MoN at ambient temperature

Parameter	X-ray	Neutron	Neutron
Space group	$P6_3mc$ (186)	$P6_3mc$ (186)	$P6_3mc$ (186)
Temperature (K)	290	290	7
a (Å)	5.7402(5)	5.73659(10)	5.73310(17)
c (Å)	5.6203(3)	5.61884(17)	5.61086(17)
Volume (Å^3)		160.133	159.71
Mo 1 x	0.0	0.0	0.0
y	0.0	0.0	0.0
z	0.6195(12)	0.556341	0.540954
U_{iso} (Å^2)	0.01769(12)	0.00509(13)	0.00484(16)
SOF	0.75(6)	1	1
Mo 2 x	0.489115(13)	0.488531(12)	0.491769(9)
y	0.510886(10)	0.511470(9)	0.508232(10)
z	0.56005(11)	0.556295(11)	0.534499(13)
U_{iso} (Å^2)	0.08512(16)	0.00151(19)	0.0011(7)
SOF	1.0(5)	1	1
N 1 x	0.333333	0.333333	0.333333
y	0.666667	0.666667	0.666667
z	0.793873(13)	0.826381(13)	0.840186(11)
U_{iso} (Å^2)	0.00219(11)	0.00464(17)	0.00385(13)
SOF	1.0(2)	1	1
N 2 x	0.147995(9)	0.167585(13)	0.164285(8)
y	0.852005(11)	0.832418(14)	0.835718(11)
z	0.264437(17)	0.298841(14)	0.322219(9)
U_{iso} (Å^2)	0.03143(14)	0.00359(10)	0.00329(14)
SOF	0.89(4)	1	1
Z	8	8	8
R_p	2.8%	4.9%	4.07%
wR_p	3.8%	5.6%	5.42%
χ^2	2.05	2.42	4.8

Results of the Rietveld analysis of the neutron diffraction patterns for the ordered phase of δ-MoN are shown in Fig. 3. Detailed in Table 1 are the crystal structure parameters obtained from the Rietveld analysis including the goodness of fit information. The site occupancy factors were refined within the analysis however they were found to be very close to unity and they were then fixed at this value. It can be seen that all of the nitrogen and molybdenum sites are fully occupied, which was not observed using X-ray diffraction information. Data were also collected below and

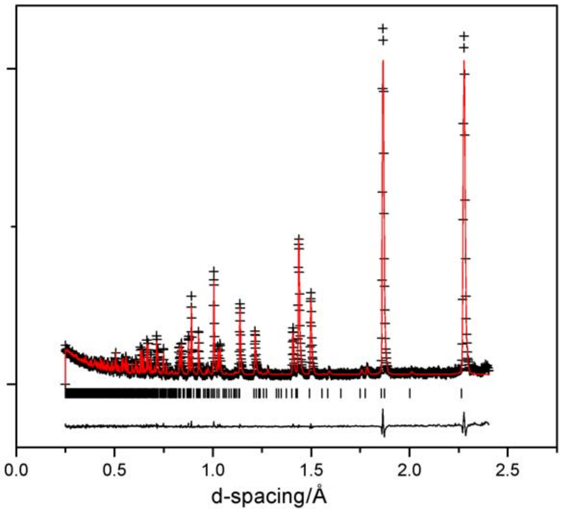

Fig. 3. The neutron observed (+) and calculated (–) profile and difference profiles (bottom trace) for δ-MoN at 290 K.

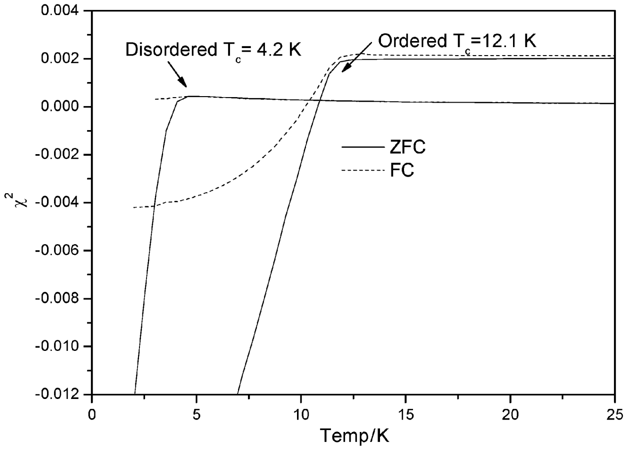

Fig. 4. The SQUID magnetometer results from 2 to 25 K and clearly shows the deviation from the ZFC and FC measurement.

above the superconducting transition however, no changes in the structure were observed, and no discontinuities in structure parameters were found as a function of temperature. We have estimated the thermal expansion to be 0.0015 Å^3 K^{-1} assuming it is linear between the two temperatures used for the diffraction measurements.

The SQUID magnetometer results for the disordered phase show that there is a superconducting transition at 4.2 K, clearly shown by the difference between the ZFC and FC data (Fig. 4). There is a large increase in the transition temperature upon high pressure annealing to 12.1 K (Fig. 4) confirming the work published previously of Bezinge [2] who showed that the superconducting transition temperature increases with time of high pressure annealing, and is thus correlated with the to ordering of the nitrogen atoms. The superconducting transition temperature of elemental Mo is 0.9 K indicating that the transitions are independent of any trace impurities. The molybdenum atoms in the ordered phase form equilateral triangle clusters stacked upon each other and sited at $z = 0.556341(10)$ and 0.056341(10). Nitrogen atoms are situated centrally between each triangular metal cluster at $z = 0.298841(14)$ (Fig. 5). There are distinct alternating hexagonal layers of molybdenum and nitrogen atoms. The interatomic distances of Mo–Mo in and between the clusters are 2.809(2) and 3.066(2) Å, respectively. The Mo–N distances range from 2.152(2) to 2.206(2) Å. At low temperature there is an observable decrease in both the lattice parameters and the bond lengths. The interatomic Mo–Mo distance in and between the clusters at 7 K is reduced to 2.805(2) and 3.008(2) Å.

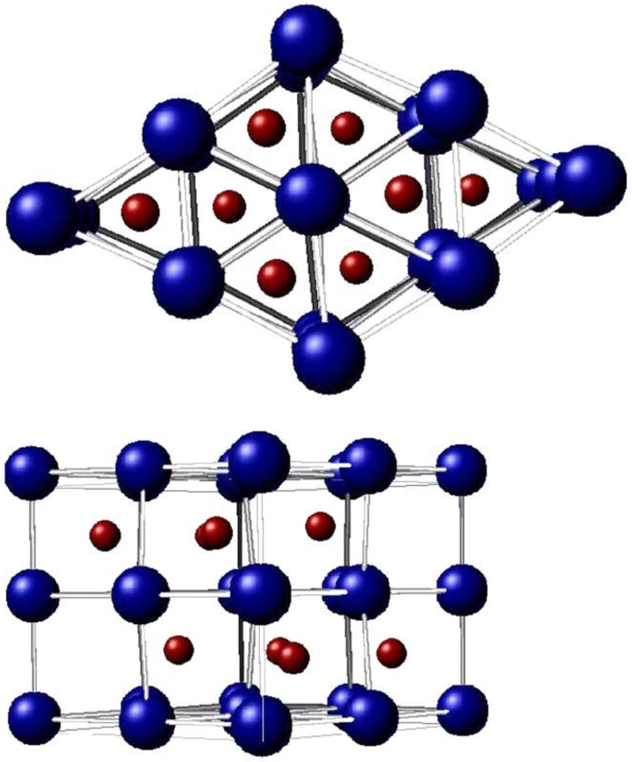

Fig. 5. Pictural representation of δ-MoN showing triangular cluster of molydenum atoms (large spheres) and the alternating hexagonal layers of molybdenum and nitrogen (smaller spheres).

4. Conclusions

We have shown that upon high pressure annealing δ-MoN transforms from a disordered to an ordered structure, which is accompanied by a unit cell doubling and an increase in the superconducting transition temperature. We have confirmed by use of TOF neutron diffraction that crystalline δ-MoN has a hexagonal structure with the $P6_3mc$ (186) space group, with a unit cell that is doubled compared with the disordered structure prepared by solid-state synthesis. The molybdenum and nitrogen atoms are ordered in the structure.

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