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**Direct Solid-State Synthesis of the Superconductor NaMo₆Se₈: Single-Crystal Structure,
Electrical and Magnetic Properties**

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Abstract

Polycrystalline samples and single-crystals of the Mo_6 cluster selenide NaMo_6Se_8 were synthesized by direct solid-state reaction at high temperature for the first time. The crystal structure was solved by X-ray diffraction on a single-crystal ($R1 = 0.0251$ and $wR2 = 0.0593$ for 911 independent reflections and 25 variable parameters). NaMo_6Se_8 crystallizes in the R-3 trigonal space group with the following parameters: $a = 9.5564$ (2) Å and $c = 11.7181$ (3) Å with 3 formulas per unit-cell. The crystal structure of NaMo_6Se_8 contains $\text{Mo}_6\text{Se}_8^{\text{I}}\text{Se}_6^{\text{a}}$ cluster units (octahedral Mo_6 cluster inscribed in a pseudo S_8 cube) separated from each other by large voids which are filled up by eight-coordinate Na atoms. The evolution of the Mo-Mo distances of the octahedral Mo_6 cluster with respect to the cationic charge in the selenide Chevrel phases is also discussed. NaMo_6Se_8 behaves as a p -type metal with relatively low electrical resistivity and becomes superconductor below 9.2 K.

Keywords

Reduced molybdenum selenides, molybdenum clusters, sodium, transport properties, superconductor.

1. Introduction

Since their discovery in 1971, the ternary molybdenum chalcogenides of general formula MMo_6X_8 ($M = Ag, Sn, Ca, Sr, Ba, Pb, 3d \text{ elements, rare-earths}$; $X = S, Se, Te$), known as Chevrel phases [1], have been extensively studied by the scientific community during 1970s and 1980 because of their outstanding physical properties as, for instance, high superconducting critical temperature T_c (up to 15 K in $PbMo_6S_8$) and high superconducting critical field H_c (up to 60 T in $PbMo_6S_8$) [2]. In the case of rare-earth containing Chevrel phases, a long-range magnetic order and a superconducting state may coexist in the same specimen [2, 3]. [4–6]. More recently, interest in Chevrel phases as thermoelectric materials began in 1997-1998, when promising thermoelectric properties were observed in the semiconducting phase $Mo_2Re_4Se_8$ by Caillat and Fleurial [7]. $NaMo_6Se_8$ was first characterized on powder samples prepared by electrochemical intercalation of Na^+ into Mo_6Se_8 by Gocke et al. and Tarascon et al. in 1987 [8, 9]. More recently, $NaMo_6Se_8$, was obtained in a yield of 62% via the topotactic reaction of the binary Mo_6Se_8 in contact with a benzophenone/ Na /THF solution (in the inert atmosphere of an Ar glovebox) as the source of Na^+ ions and as the reducing agent [10]. In the same paper, the authors also presented the crystal structure determined from X-ray data collected on a multiphasic sample. We describe here the direct solid-state powder synthesis as well as the crystal growth of $NaMo_6Se_8$ samples. Single crystal resistivity and magnetic measurements are also presented. The results of the current structural determination on single crystal show a great amelioration in the accuracy of the interatomic distances and all atoms could be refined anisotropically. On the other hand, single crystal resistivity and powder magnetic susceptibility measurements indicate, for the first time, that $NaMo_6Se_8$ becomes superconducting below 9.2 K.

2. Experimental

2.1 Synthesis and Crystal Growth

Starting materials used for the solid-state syntheses were $MoSe_2$, $Na_2Mo_6Se_6$, and Mo , all in powder form. Before use, Mo powder was reduced under H_2 flowing gas at $1000^\circ C$ during ten

hours in order to eliminate any trace of oxygen. The molybdenum diselenide was prepared by the reaction of selenium with H₂ reduced Mo in a ratio 2:1 in an evacuated (ca. 10⁻² Pa Ar residual pressure) and flame-baked silica tube, heated at about 700°C during two days. Na₂Mo₆Se₆ were prepared in two steps. In the first one, In₂Mo₆Se₆ was obtained from a stoichiometric mixture of powders of MoSe₂, InSe, and molybdenum heated at 1000°C during 36 hours in sealed evacuated silica ampule. In the second step, an ion exchange reaction was performed between In₂Mo₆Se₆ and NaCl at 800°C. In the latter reaction, a powder mixture of In₂Mo₆Se₆ and NaCl in the 1:2.5 ratio was cold pressed. Subsequently, the cylindrical pellet was introduced and sealed under vacuum in a silica tube (l ~250 mm, Ø ~ 20 mm). The pellet was placed at one end of the silica tube in a furnace that was heated at 800°C for 48 h while the other extremity of the tube was about 8 cm out from the furnace and thus at about the room temperature. After reaction, white InCl crystals were observed at the cool end of the tube while powder X-ray diffraction diagram of the pellet reveals a pure powder of Na₂Mo₆Se₆. Additionally, all starting materials were stored and handled in an argon-filled glove box to avoid contamination by oxygen and moisture. Monophasic powder samples of NaMo₆Se₈ (~10 g) were prepared from the required stoichiometric mixture of Na₂Mo₆Se₆, Mo, and MoSe₂ heated at 1300 °C during 40 hours in a molybdenum crucible sealed under a low argon pressure using an arc-welding system. An X-powder diagram (CuKα₁ radiation) of the resulting product is shown in Figure 1. Single crystals of NaMo₆Se₈ were obtained by heating a powder sample at 1750°C for 3 hours, then cooled at 100 °C/h down to 1000°C and finally furnace cooled to room temperature.

2.2 Single Crystal Structure Determination

The intensities were collected on a single crystal using a Nonius Kappa CCD diffractometer equipped with a graphite-monochromator (Mo-Kα radiation, λ = 0.71073 Å) at 20 °C. As the primitive rhombohedral unit cell (a = 6.7668 (5) Å, a = 90.02 (1)) was very close to a cubic cell, it was not possible to collect the data in the hexagonal unit since the ‘true’ 3-fold axis was not known at this stage. The COLLECT program package [11] was employed to establish the angular scan conditions (φ and ω scans) used in the data collection that was made in the P-1 space group. The data set was processed using EvalCCD [12] for the integration procedure. An

absorption correction was performed using the analytical method described by de Meulenaar and Tompa [13] from description of the crystal faces. The crystal structure was first solved by the direct methods using the software SIR2008 [14] and refined using the program SHELXL97 [15] in the P-1 space group. Subsequently, analysis of the structure with the ADDSYM routine in the PLATON package [16] allowed us to transform the data in the hexagonal setting of the R-3 space group. Refinement of the site occupancy factor of the Na site led to a value of 1.03(3) and thus to a full occupation. Crystallographic data and X-ray structural analysis for NaMo_6Se_8 are recapitulated in Table 1. The final atomic coordinates, and the equivalent isotropic displacement parameters are given in Table 2, and selected interatomic distances are listed in Table 3. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-1881644.

2.3 Electrical Resistivity Measurements

The temperature dependence of the electrical resistivity was studied on a single crystal of NaMo_6Se_8 along the *c* axis. The conventional four-probe AC technique was used with a current amplitude of 0.1 mA. The four contacts were ultrasonically welded with molten indium onto a single crystal previously checked on a Nonius Kappa CCD diffractometer. The ohmic behavior and phase invariance were verified during measurements.

2.4 Magnetic susceptibility measurements

Magnetic susceptibility data were gathered on cold pressed powder samples of about 100 mg using a Quantum Design SQUID magnetometer in the temperature range 2 - 20 K under an applied field of 0.1 T.

3. Results and Discussion

NaMo_6Se_8 belongs to the trigonal Chevrel-phases type compounds having the general formula MMo_6X_8 with M being is a large cation such as alkali metal, alkaline earth, lanthanide, actinide and X, a chalcogen (S, Se, Te) [see, for instance, Chevrel & Sergent (1982)]. Therefore, the NaMo_6Se_8 crystal structure, shown in Figure 2, is based on octahedral Mo_6 clusters whose surroundings consist of fourteen selenium atoms, eight of them form a distorted cube (i-type ligands) and the six others cap the faces of the Se_8 cube (a-type ligands) (Figure 3). In the structure of NaMo_6Se_8 , six of the i-type chalcogen atoms of the $\text{Mo}_6\text{Se}_8^i\text{Se}_6^a$ unit are shared with adjacent units with the connective formula $\text{Mo}_6\text{Se}_2^i\text{Se}_6^{i-a}\text{Se}_6^{a-i}$ to create the three-dimensional Mo—Se array. The center of the Mo_6Se_8 cluster unit corresponds to the Wyckoff position 6b and thus, the Mo_6 cluster have the -3 symmetry. In the Mo_6 cluster, the Mo—Mo bond lengths are 2.6836 (5) Å between the Mo atoms related through the threefold axis also called intra-triangle distances and noted $(\text{Mo-Mo})_\Delta$ and 2.7601 (6) Å for the Mo-Mo distances between Mo atoms of two different superimposed Mo_3 triangles perpendicular to the threefold axis and noted $\text{Mo}_\Delta\text{-Mo}_\Delta$. In the previous refinement on a powder sample, the latter two distances are 2.711 and 2.769 Å, respectively. A survey of accurate crystal structures made on the selenide Chevrel-phases with the ICSD data base shows that the $(\text{Mo-Mo})_\Delta$ distances are around 2.68-2.70 Å while the $\text{Mo}_\Delta\text{-Mo}_\Delta$ distances range from about 2.72 to 2.837 Å. The increase of the $\text{Mo}_\Delta\text{-Mo}_\Delta$ inter-triangle distances is indeed correlated to the decrease of the cationic charge towards the Mo_6 cluster, and thus to the metallic electron count MEC (i.e. the number of electrons per Mo_6 cluster) which decreases from about 23-24 electrons for the shortest $\text{Mo}_\Delta\text{-Mo}_\Delta$ distances (around 2.73 Å) to 20 electrons in the binary Mo_6Se_8 in which the inter-triangle distances $\text{Mo}_\Delta\text{-Mo}_\Delta$ is 2.837 Å (Figure 4). This is in agreement with previous theoretical calculations, made on the compounds $\text{In}_x\text{Mo}_{15}\text{S}_{19}$ [17] and $\text{Ag}_3\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ [18] containing Mo_6 and Mo_9 clusters in equal proportion, which show that the intra-triangle distances $(\text{Mo-Mo})_\Delta$ are weakly antibonding while the inter-triangle distances $\text{Mo}_\Delta\text{-Mo}_\Delta$ are bonding. Each Mo atom is surrounded by five Se atoms (4 Se1 and 1 Se2) forming a distorted square-based pyramid with Mo-Se distances ranging from 2.5158(6) Å to 2.6793(5) Å. The apex of the pyramid is shared with a neighboring Mo_6 cluster and therefore ensures three-dimensional cohesion. Consequently, each Mo_6Se_8 unit is linked to 6 adjacent Mo_6Se_8 units to generate the Mo—Se network. This arrangement leads to the shortest Mo-Mo distances between neighboring Mo_6 clusters being 3.4243 (5) Å, indicating only weak Mo-Mo interactions between adjacent Mo_6 units. Na^+ cations occupy a large distorted cubic site formed by the chalcogen atoms of eight different Mo_6Se_8 units and often referenced as cavity 1 (Figure

5). This confirms the assumptions made in previous works and particularly in Ref 10 in which the Na position was deduced from bond valence sum considerations. They are surrounded by two Se2 atoms at a distance of 2.7348(7) Å and six Se1 atoms at 3.2187 (4) Å instead of 2.681 and 3.136 Å in ref. 10.

The electrical resistivity of a single-crystal of NaMo₆Se₈ as a function of the temperature is shown in Figure 6. NaMo₆Se₈ presents a metallic behavior, with a room temperature resistivity of about 4.1 10⁻⁴ Ω.cm. Below 9.2 K, NaMo₆Se₈ becomes superconductor with a resistivity of about 4 10⁻⁵ Ω.cm just before the superconducting transition. Superconductivity was also confirmed by Meissner effect from susceptibility measurements on a powder sample (Figure 7). The critical temperature (T_c) of NaMo₆Se₈ is slightly higher than that observed for the other selenide containing a monovalent cation AgMo₆Se₈ that has a T_c of 5.9 K [2]. In the selenides, the highest T_c is 11.4 K observed for LaMo₆Se₈ [2].

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Table Captions:

Table 1. Crystal data and structure refinement for NaMo₆Se₈.

Table 2. Fractional atomic coordinates, equivalent isotropic displacement parameters (\AA^2), and Wyckoff positions for NaMo₆Se₈.

Table 3. Selected interatomic distances (in \AA) for NaMo₆Se₈.

Table 1. Crystal data and structure refinement for NaMo₆Se₈.

Empirical formula	NaMo ₆ Se ₈
Formula weight	1230.31
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Trigonal, R-3:H
Unit cell dimensions	a = 9.5564(2) Å, c = 11.7181(2) Å
Volume	926.78(4) Å ³
Z, Calculated density	3, 6.613 Mg/m ³
Absorption coefficient	29.456 mm ⁻¹
F(000)	1605
Crystal size	0.131 x 0.037 x 0.033 mm
Theta range for data collection	4.262 to 29.927 deg.
Limiting indices	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected / unique	6779 / 618 [R(int) = 0.0549]
Completeness to theta	99.7 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	618 / 0 / 24
Goodness-of-fit on F ²	1.241
Final R indices [I > 2σ(I)]	R1 = 0.0228, wR2 = 0.0563
R indices (all data)	R1 = 0.0239, wR2 = 0.0569
Largest diff. peak and hole	2.242 and -1.085 e. Å ⁻³

Table 2. Fractional atomic coordinates, equivalent isotropic displacement parameters (\AA^2), and Wyckoff positions for NaMo_6Se_8 .

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)$	<i>Wyckoff</i>
Mo	0.16945(4)	0.01581(4)	0.09747(3)	0.00754(12)	18f
Se1	0.32823(4)	0.03381(5)	-0.08287(3)	0.00969(12)	18f
Se2	0.0000	0.0000	0.26662(6)	0.01136(16)	6c
Na	0.0000	0.0000	0.5000	0.0438(16)	3b

Table 3. Selected interatomic distances (in Å) for NaMo₆Se₈.

Mo-Mo (x2)	2.6836(5)
Mo-Mo (x2)	2.7601(6)
Mo-Se2	2.5158(6)
Mo-Se1	2.5566(5)
Mo-Se1	2.5799(5)
Mo-Se1	2.6084(5)
Mo-Se1	2.6793(5)
Na-Se2 (x2)	2.7348(7)
Na-Se1 (x6)	3.2187(4)

Figure Captions

Figure 1. Rietveld refinement of the powder X-ray diffraction diagram for NaMo_6Se_8 . The experimental data are shown in red and the calculated profile is represented in solid black line. The difference profile between the theoretical and experimental patterns is represented in blue. The vertical blue ticks indicate the Bragg reflection positions.

Figure 2. View of the crystal structure of NaMo_6Se_8 along the $[110]$ direction (the thermal ellipsoids are drawn at the 97 % probability level).

Figure 3. The Mo_6 cluster with its Se environment (the thermal ellipsoids are drawn at the 97 % probability level).

Figure 4. Evolutions of the Mo-Mo distances within the Mo_6 cluster in the selenide Chevrel phase as a function of the cationic charge.

Figure 5. Selenium environment of the Na^+ cation. Thermal ellipsoids are drawn at the 97 % probability level.

Figure 6. Temperature dependence of the electrical resistivity ρ of a NaMo_6Se_8 single-crystal.

Figure 7. Temperature dependence of the magnetic susceptibility of NaMo_6Se_8 below 20 K.

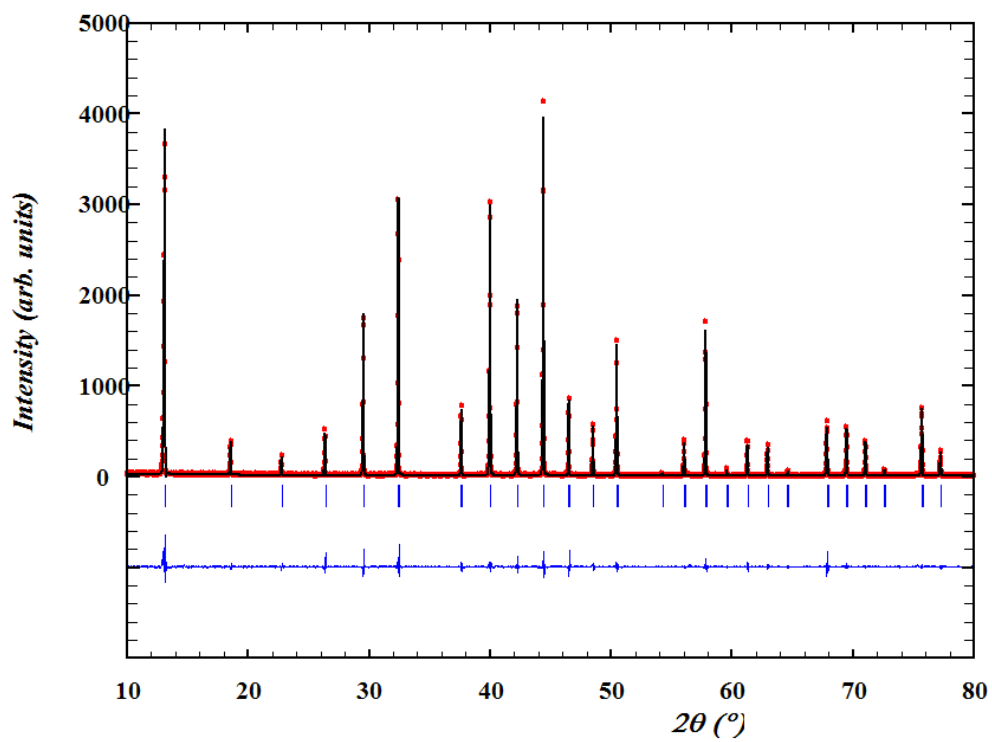


Figure 1. Rietveld refinement of the powder X-ray diffraction diagram for NaMo₆Se₈. The experimental data are shown in red and the calculated profile is represented in solid black line. The difference profile between the theoretical and experimental patterns is represented in blue. The vertical blue ticks indicate the Bragg reflection positions.

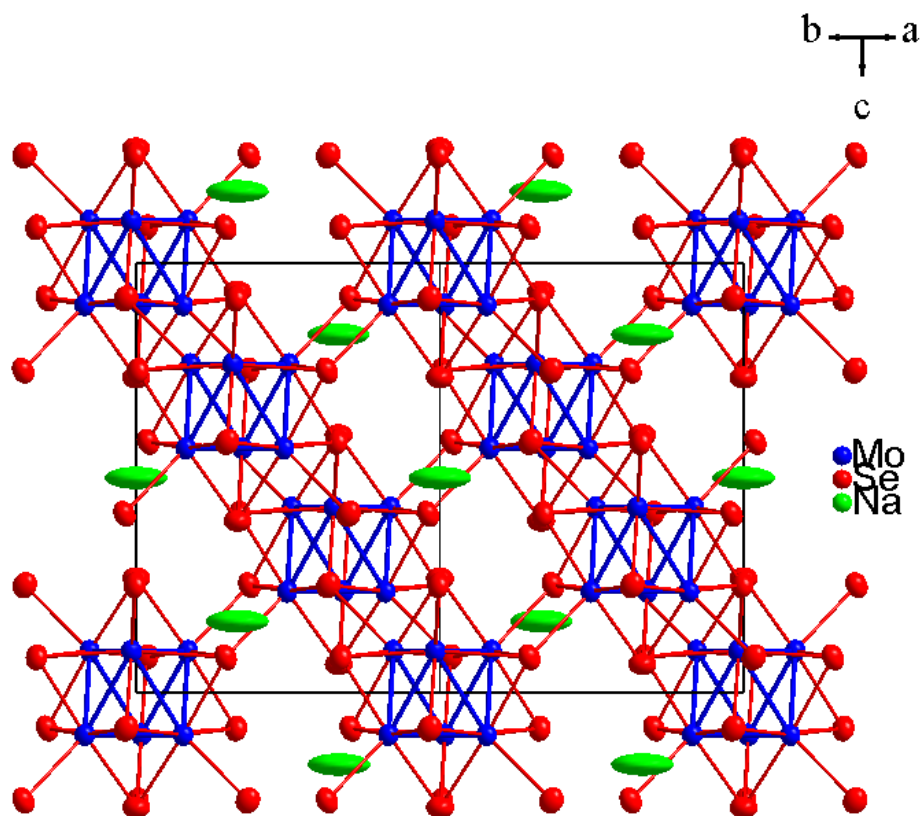


Figure 2. View of the crystal structure of NaMo₆Se₈ along the [110] direction (the thermal ellipsoids are drawn at the 97 % probability level).

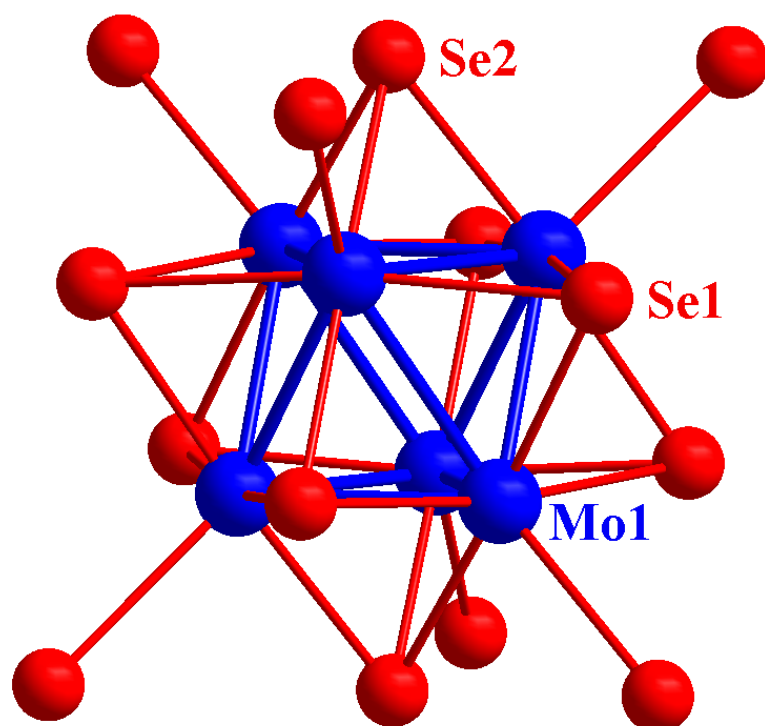


Figure 3. The Mo₆ cluster with its Se environment (the thermal ellipsoids are drawn at the 97 % probability level).

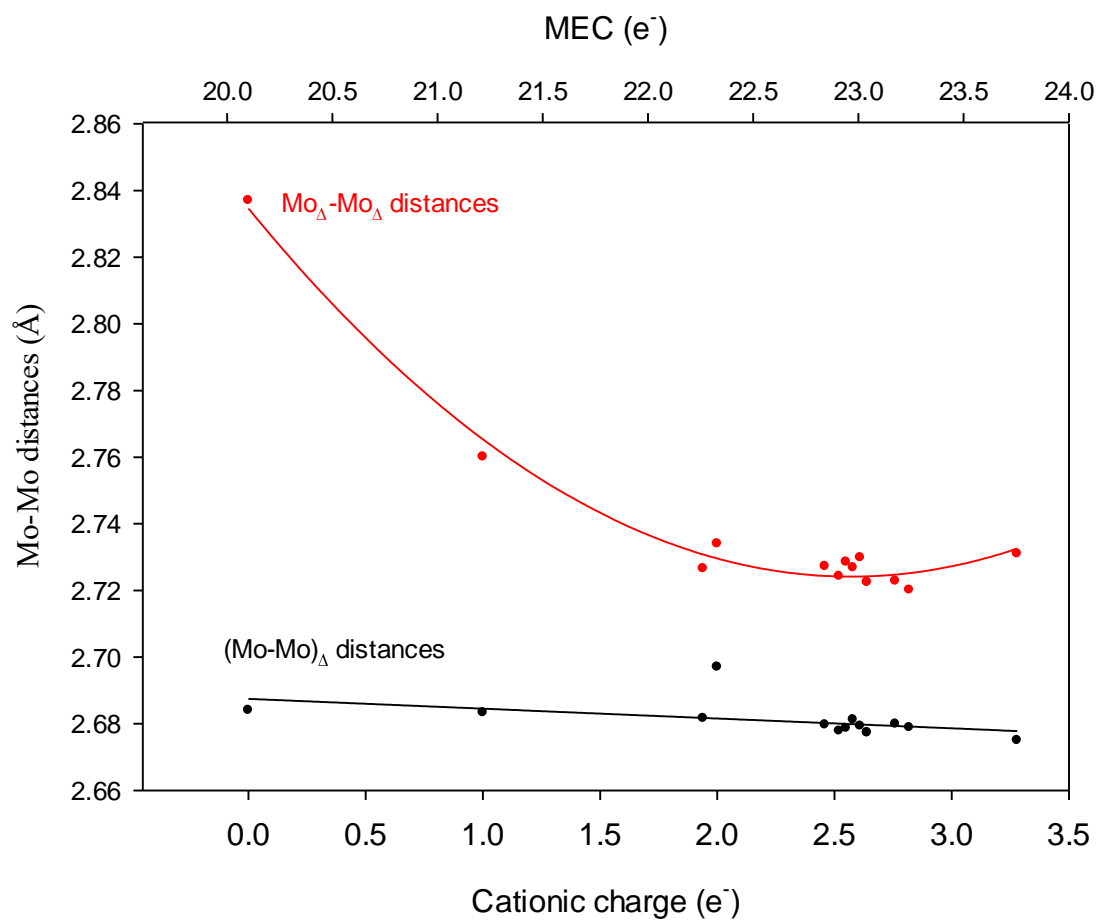


Figure 4. Evolutions of the Mo-Mo distances within the Mo₆ cluster in the selenide Chevrel phase as a function of the cationic charge.

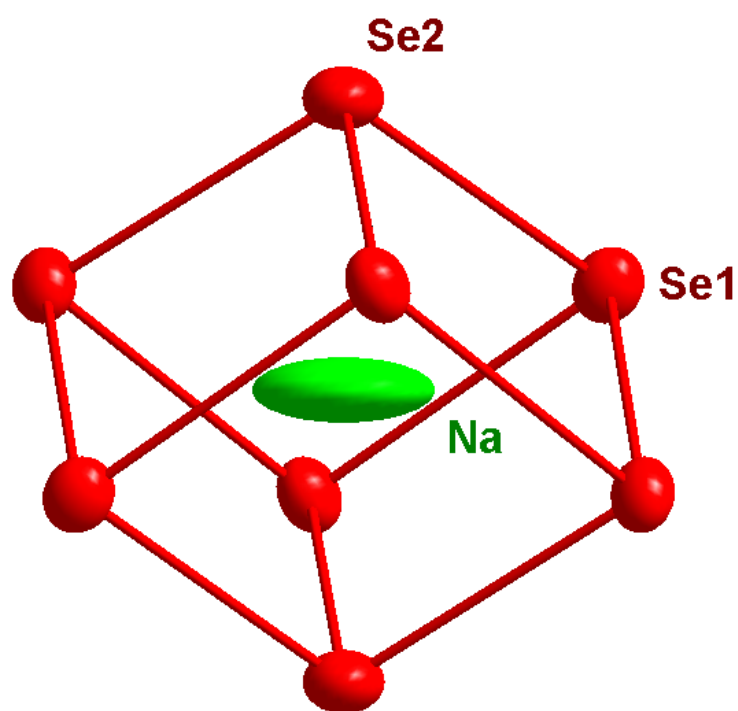


Figure 5. Selenium environment of the Na^+ cation. Thermal ellipsoids are drawn at the 97 % probability level.

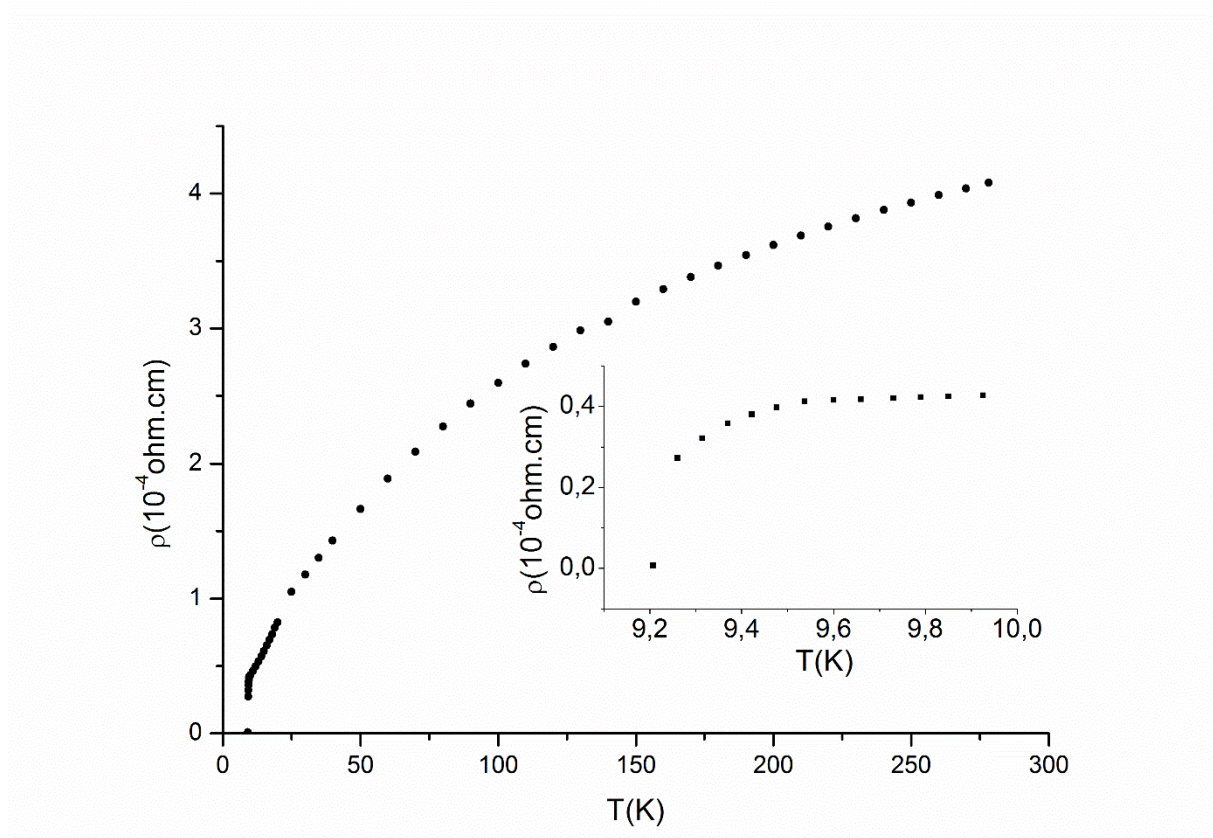


Figure 6. Temperature dependence of the electrical resistivity ρ of a NaMo_6Se_8 single-crystal.

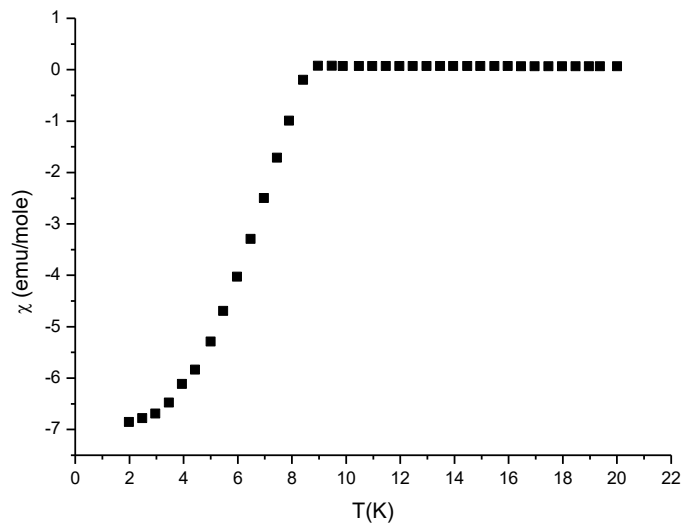
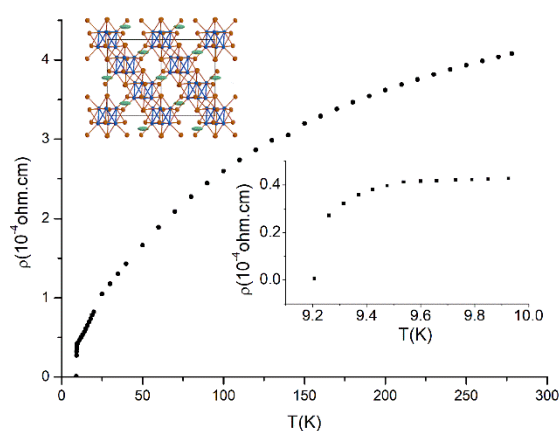


Figure 7. Temperature dependence of the magnetic susceptibility of NaMo_6Se_8 below 20 K.

Graphical abstract

The crystal structure of the cluster compound NaMo_6Se_8 contains octahedral Mo_6 forming $\text{Mo}_6\text{Se}_8^i\text{Se}_6^a$ cluster units separated from each other by large voids filled by Na atoms. Measurements of the electrical resistivity, and magnetic susceptibility revealed that NaMo_6Se_8 behaves as a *p*-type metal with relatively low electrical resistivity and becomes superconductor below 9.2.



Highlights

- Successful synthesis of single-crystalline and polycrystalline NaMo_6Se_8
- Crystal structure contains octahedral clusters
- NaMo_6Se_8 is a *p*-type metal with low electrical resistivity and superconducting below 9.2 K