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Superconductivity and structure of η-Mo_3C_2

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ABSTRACT

Local structure of the layered superconductor η-Mo_3C_2 (T_c = 8.5 K) was studied by a neutron diffraction method. The structure comprises a triangular-lattice layer and a block layer, and the layers share a common structure basis of octahedral CMo_6. We found that the block layer contains non-trivial disorders likely caused by inhomogeneous carbon distribution, while the triangular-lattice layer consists of almost perfect regular octahedra. Thus, the triangular-lattice is probably responsible for the superconductivity.

1. Introduction

Superconductivity of η-Mo_3C_2 was reported in the mid 60s [1–3], however details of structure and superconducting properties were unrevealed thus far within our best knowledge. Probably, complicated issues in regard to chemical inhomogeneity and substantial impurities disturbed progress of basic studies of η-Mo_3C_2 for nearly five decades. Recently, we found that a high pressure/temperature synthesis was effective to solve the long-term problem to some extent [4]. The method was remarkable in quality improvement of polycrystalline η-Mo_3C_2, and thus the sample somehow allowed structure refinements analysis and physical properties measurements. Although the best quality sample still contained ~13% weight fraction of α-Mo_2C, the data clearly established superconductivity at 8.5 K [4].

We conducted a neutron diffraction study on the best quality sample to date, and analysis on the neutron data uncovered structure properties of η-Mo_3C_2. In this paper, we report local structure details of η-Mo_3C_2 and compare the structure to that of the significantly related superconductor $MgCNi_3$ [5]. Since η-Mo_3C_2 has a triangular-lattice basis, thus a possibility appears that η-Mo_3C_2 shares principal physics with the water intercalated Co oxide superconductor in terms of mechanism of the unusual superconductivity [6].

2. Experimental

Experiment details were reported in Ref. [4]. A brief summary follows: starting mixtures of molybdenum and carbon fine powders at ratios of Mo/C = 3/3, 3/2, 3/1.9, and 3/1.8 were each set in a Ta capsule with a h-BN inner, followed by heating at 1700 °C for 1 h in a high-pressure apparatus, which is capable of maintaining 6 GPa during the heating. Before releasing the pressure, the capsule was quenched in the apparatus. The polycrystalline sample was studied by a neutron method in BT-1 high-resolution diffractometer at the NIST Center for Neutron Research. A Ge(3 1 1) monochromator, λ = 2.0787(2) Å, was used for data correction at room temperature. We used GSAS software for the neutron data analysis [7,8].

3. Results and discussion

Fig. 1 shows superconducting transition of the η-Mo_3C_2 compound prepared under the high-pressure/temperature condition. The magnetic data are consistent with the electrical data in regard to phenomenology of bulk superconductivity [4]. While the magnetic transition is 8.5 K, a thermodynamically transition (specific heat data) is 7.4 K [4]: The small deviation is probably due to inhomogeneity of carbon distribution, as discussed in Ref. [4]. Superconducting volume of loose powder of the sample was estimated ~100% in the zero-filed-cool condition and ~16% in the field-cool condition (at 2 K), clearly rejecting a possibility of contributions from impurities.

The superconducting η-Mo_3C_2 compound was also studied by a neutron diffraction method. To the best of our knowledge, it was conducted for the first time. Details of the result were summarized

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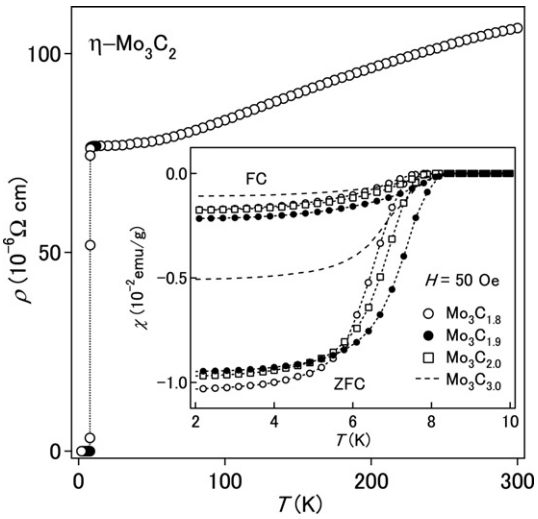

Fig. 1. Electrical resistivity and magnetic susceptibility of the polycrystalline sample of η-Mo_3C_2. Both data were taken from Ref. [4].

elsewhere [4]: space group was $P6_3/mmc$, and lattice parameters were $a = 3.0131(1)$ Å and $c = 14.637(1)$ Å. Cell volume was 115.08(1) Å^3, and estimated density was 8.986 g/cm^3. The optimized atom positions were Mo1 [2*b*; 0, 0, 1/4], Mo2 [4*f*; 1/3, 2/3, 0.08619(8)], C1 [2*a*; 0, 0, 0], and C2 [4*f*; 1/3, 2/3, 0.67093(14)]. Mo and C have two crystallographic sites each and Mo sites were assumed to be fully occupied in the analysis. Estimated occupancy factor for carbon was 0.94(2) at C1 site and 0.51(1) at C2 site.

The structure of η-Mo_3C_2 was drawn from the neutron results, and a cross-sectional view is shown in Fig. 2. Each carbon is coordinated by six Mo atoms, forming an octahedral CMo_6. The octahedron at C1-site shares the edge with neighbor octahedra and forms a layer. The C1-Mo_6 layer stacks up with a C2-site block along *c*-axis, alternatively. We should keep it in mind that approximately half of carbons at C2 site are missed, while C1 site is nearly full-occupied: The selective distribution may enhance possible anisotropy of superconducting properties because such the disorder must weaken superconducting correlations. The possibility can be evaluated if a high-quality single crystal becomes available.

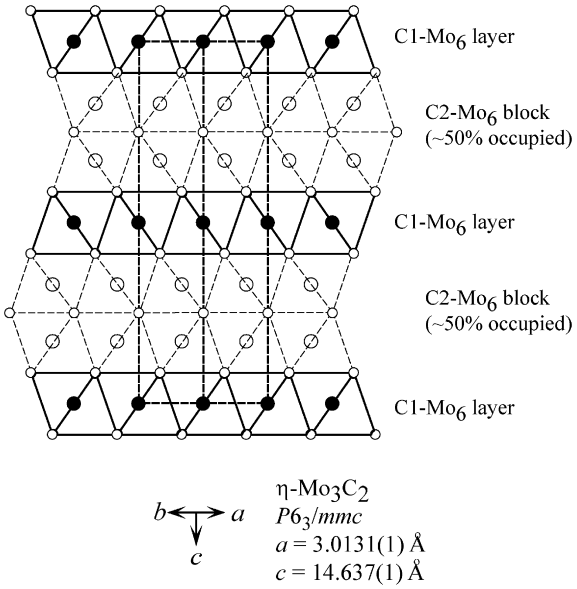

Fig. 2. Schematic stricture view of η-Mo_3C_2. The numerical data were reported in Ref. [4]. solid and open circles represent carbon at C1 and C2 sites, respectively. Small open circle denotes molybdenum.

Fig. 3a shows a top-down view of the structure of η-Mo_3C_2 (*c*-axis is perpendicular to the page), clearly showing a triangular-lattice. A possibility thus appears that the triangular symmetry plays a key role in mechanism of the superconductivity; such a scenario is intensively discussed in Refs. [9–11] in the context of frustrated superconductors. In order to shed more light on the possibility, we compare the lattice with that of the related superconductor $MgCNi_3$. A corresponding view of $MgCNi_3$ is shown in Fig. 3b. It is clear that both compounds share a common structure basis, a metal-coordinated carbon octahedron; i.e., CMo_6 for η-Mo_3C_2 and CNi_6 for $MgCNi_3$. Although the triangular-lattice

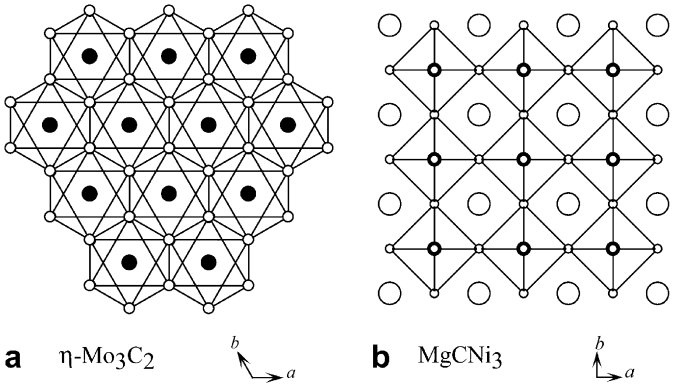

Fig. 3. Comparison between: (a) the triangular-lattice of η-Mo_3C_2, and (b) the square lattice of $MgCNi_3$. Small open circle denotes molybdenum/nickel. Solid circle denotes carbon. Large open circle denotes magnesium.

Table 1
Comparison of superconducting parameters of η-Mo_3C_2 and of $MgCNi_3$ (taken from Ref. [4])

Parameters	Unit	η-Mo_3C_2	$MgCNi_3$
T_c	K	7.4	7.6
$H_{c1}(0)$	T	0.014	0.010
$H_c(0)$	T	0.15	0.19
$H_{c2}(0)$	T	5.7	14.4
$\lambda(0)$	nm	197	248
$\xi(0)$	nm	7.6	4.6
$\kappa(0)$		26	54
γ	mJ mol^{-1} K^{-2}	11.8	30.1
$\Delta C\,\gamma^{-1}\,T_c^{-1}$		1.48	2.1

Table 2
Selected bond distances and angles of η-Mo_3C_2. The data were calculated from the atomic coordinates determined by a neutron diffraction study at room temperature (Ref. [4])

Atoms	Coordination number	Distance (Å) or angle (°)	Atoms	Angle (°)
Mo1–Mo1	6	3.01313(14)	C2–Mo1–C2	130.800(28)
Mo1–Mo2	6	2.9623(9)	C1–Mo2–C1	89.027(34)
Mo1–C2	6	2.0895(11)	C1–Mo2–C2	90.643(32)
Mo2–Mo1	3	2.9623(9)	C1–Mo2–C2	179.539(1)
Mo2–Mo2	6	3.01313(14)	C2–Mo2–C2	89.68(8)
Mo2–Mo2	3	3.0647(18)	Mo2–C1–Mo2	89.027(34)
Mo2–C1	3	2.1489(6)	Mo2–C1–Mo2	90.973(34)
Mo2–C2	3	2.1365(14)	Mo2–C1–Mo2	180
C1–Mo2	6	2.1489(6)	Mo1–C2–Mo1	92.28(6)
C2–Mo1	3	2.0895(11)	Mo1–C2–Mo2	89.004(17)
C2–Mo2	3	2.1365(14)	Mo2–C2–Mo2	89.68(8)
C2–Mo1–C2		92.28(6)	Mo1–C2–Mo2	178.15(10)
C2–Mo1–C2		67.27(9)		

The site occupancy factors were 0.935(23) and 0.514(13) for C1 and C2 sites, respectively.

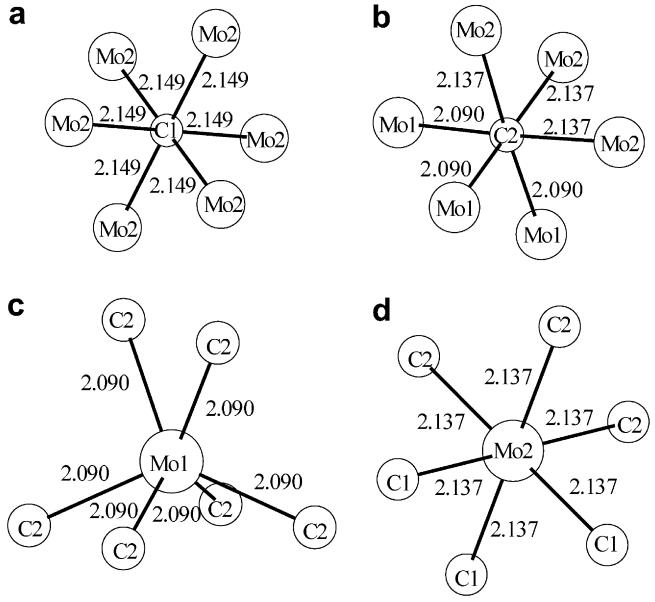

Fig. 4. Coordination environment of (a) C1, (b) C2, (c) Mo1, and (d) Mo2 atoms of η-Mo_3C_2. Numbers are bond distance in angstrom (Å).

highly contrasts with the square lattice, both compounds show quantitatively similar type-II superconductivity (see Table 1). Therefore, it is an open question if arrangement of the octahedra in the triangular symmetry is crucial in mechanism of the observed superconductivity. Further studies would be needed to sort out principal physics of the triangular-lattice superconductivity.

Further investigation follows for the triangular-lattice of η-Mo_3C_2. Bond distances and angles are calculated from the neutron data, and selected those are shown in Table 2. Local coordination of each atom is sketched out in Fig. 4a–c. At first, let us see the C1–Mo_6 octahedra: all bonds between C1 and Mo atoms are exactly identical at 2.149 Å and all bond angles are either 89–91° or 180°, indicating that the C1–Mo_6 octahedron is nearly a perfect regular octahedron. As a result, distortion factor (defined as the ratio of the longest to the shortest distance) of 1.000 for the C1–Mo_6 octahedron is much smaller than ~1.023 for the C2–Mo_6 octahedron. The distortion in the C2 site block is probably a consequence of the carbon non-stoichiometry.

With all facts above in mind, a general picture for copper oxide superconductors in regard to classification into charge reservoir blocks and superconducting layers seems likely applicable to η-Mo_3C_2. The possible analogous picture comprises the charge reservoir C2 block and the superconducting triangular-lattice layer is phenomenologically consistent with the result that superconducting transition temperature of η-Mo_3C_2 depends on the carbon concentration [4].

In summary, we studied the triangular-lattice of the layered superconductor η-Mo_3C_2 by a neutron diffraction method. We found that the triangular-lattice consists of an almost perfect regular octahedron CMo_6, while the C2 block contains non-trivial disorders include carbon vacancies and octahedron distortions. Although the triangular-lattice is probably significant for superconductivity, a role of the lattice symmetry is, however, unclear in mechanism of the observed superconductivity. Nevertheless, the compound η-Mo_3C_2 likely provides valuable opportunities for studies of physics of triangular-lattice superconductivity.

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