New Helical Chain Structure for Scandium at 240 GPa [1]

Studies of the 3*d* transition metals at high-pressure have attracted attention for a variety of reasons, such as the interest in structural phase transitions induced by electronic transitions, their natural magnetic character and because they are major components of the Earth's core. At present, these metals are considered to exhibit a systematic structure sequence of pressure-induced phase transitions due to electron transfer from the s-band to the d-band under pressure (the so-called *s-d* transition): hcp - bcc - hcp - fcc [2].

However, our recent X-ray study of titanium (Ti) revealed that its structural sequence is different from the canonical sequence, that is, the hcp phase, with increasing pressure, transforms to the ω phase with a host-guest structure, and furthermore, rather anisotropic structures consisting of zigzag chains (see Fig. 1) occur in the high-pressure phases above 100 GPa [3]. Why does such an anisotropic structure occur under high pressure? We hypothesize that the large radius of the 3*d* electron orbital of Ti may be a key in the reason behind the structural stability.

Scandium (Sc) is the first member of the 3*d* transition elements and neighbors Ti. Its 3*d* electron orbital has a larger radius than that of Ti. In order to test our hypothesis, the structure of Sc was investigated under high pressure. In this work, X-ray diffraction experiments of Sc were carried out over a wide range of pressures, up to 300 GPa using a monochromatic synchrotron radiation source on beamline **BL10XU**.

From our experiments, four structural phase transitions were found. Each high-pressure phase was assigned in order of pressure to Sc-II, III, IV and V, respectively. The first transition from hcp (Sc-I) to Sc-II was observed at 23 GPa. The structure of Sc-II has been explained as a tetragonal lattice comprising a host lattice and a guest lattice [4]. The other three phase transitions occurred at pressures of 104, 140 and 240 GPa, respectively. The profiles of Sc-III, IV and V consist of a large number of diffraction lines and suggest that the structures of these phases are not Braves lattices, but are complicated structures. Namely, these structures do not follow the predicted sequence.

The transition to Sc-V was sharp and almost complete at 244 GPa. This high-pressure phase was stable up to 300 GPa. The diffraction profile of Sc-V shown in Fig. 2 is completely indexed on the basis of the 6 screw hexagonal lattice with this S.G or its enantiomorph. The relative intensities were well explained by this structure with six Sc atoms in the 6*a* Wyckoff positions with 0.461 and with an *R* factor of $R_{wp} = 25\%$. The structure of Sc-V shown in Fig. 3 consists of infinite 6 screw chains parallel to the *c* axis. The Sc atoms have two nearest-neighbor atoms with an intra-chain distance of 2.05 Å. The nearest-
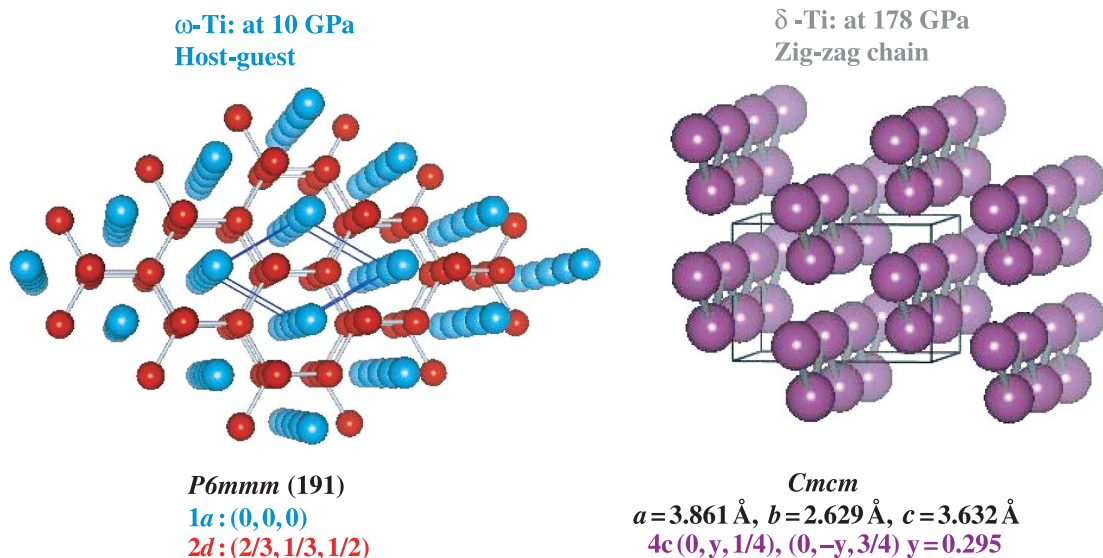
ω-Ti: at 10 GPa
Host-guest

δ -Ti: at 178 GPa
Zig-zag chain

P6mmm (191)
1*a* : (0, 0, 0)
2*d* : (2/3, 1/3, 1/2)

Cmcm
$a = 3.861\,Å,\ b = 2.629\,Å,\ c = 3.632\,Å$
4c (0, y, 1/4), (0, –y, 3/4) y = 0.295

Fig. 1. Structures of high-pressure phases of titanium (Ti) metal: ω-Ti at 10 GPa and δ-Ti at 178 GPa.

Sc-V at 242 GPa

Hexagonal S.G. $P6_122$ (or $P6_522$)
$a = 2.353(1)$ Å, $c = 10.445(3)$ Å, $V_A = 8.36$ Å^3
$6a (x, 0, 0)$ Å, $x = 0.461(2)$, $Z = 6$

Intensity (arb. unit)

102
100
101
103
006
104
105
106
110
112
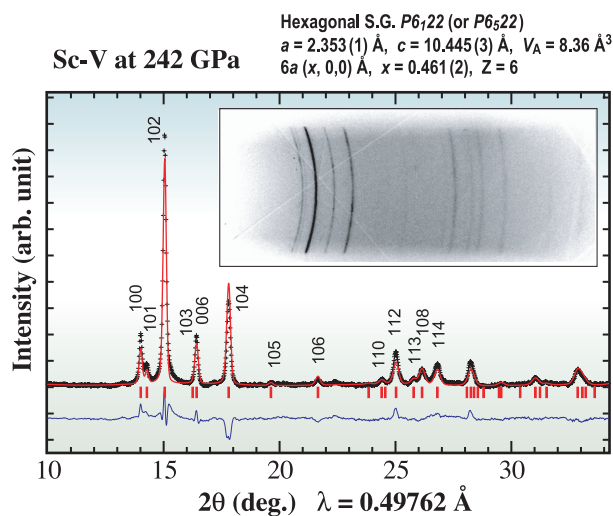113
108
114

2θ (deg.) $\lambda = 0.49762$ Å

Fig. 2. Powder diffraction profile of the highest pressure phase of Sc, Sc-V, at 242 GPa, together with the diffraction image. The profile is completely indexed on the basis of the hexagonal $P6_122$ or $P6_522$ lattice. The solid red line represents the Rietveld fit.

neighbor distance between chains is 2.155 Å, which is 5% longer than in the intra-chain distance.

On the basis of the above results, an anisotropic chain-like structure also occurs in Sc. The nearest-neighbor distance between Sc atoms is 2.05 Å. Considering the radius of 1.24 Å of the $3d$ electron state of the Sc atom, as quoted by Harrison [5], the atomic distance means that the $3d$ orbitals of an Sc atom overlap with those of the neighbor atoms in the chain (Table 1). This suggests that the $3d_{zz}$-orbital localized near the inner core is hybridized with the $4s$-orbital, and directional covalent bonding between the hybridized orbitals results in the anisotropic chain-like structure. In conclusion, the present observation provides not only evidence supporting our hypothesis but also a new viewpoint for understanding the structural stability of the transition metals under extremely high pressures, that is, the importance of interactions among the $3d$ orbitals of nearest-neighbor atoms.
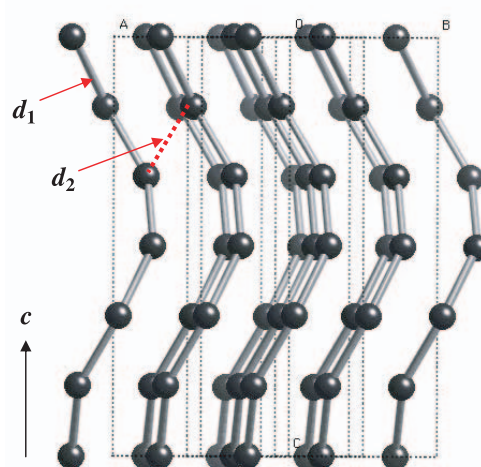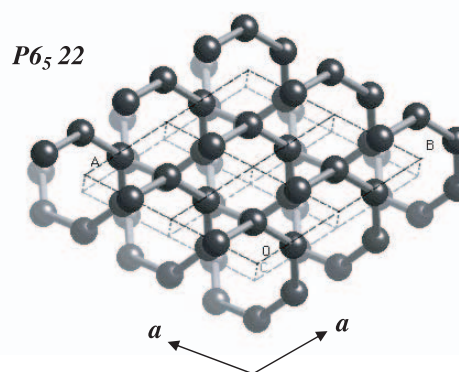

$P6_522$

a ⟵ ⟶ a

d_1
d_2

c

Fig. 3. Structure of the Sc-V phase at 242 GPa on the basis of the $P6_122$ lattice. The structure consists of infinite 6_1 chains parallel to the c axis. The intra-chain and inter-chain distances, d_1 and d_2 are 2.051 Å and 2.155 Å, respectively.

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Table 1. Radius of $3d$ orbital: r_d (Å) by W.A. Harrison [5].

Sc	Ti	V	Cr	Mn	Fe	Co	Ni
1.24	1.08	0.98	0.90	0.86	0.80	0.76	0.71

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